The Theories of Chemistry

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THE THEORIES

OF

CHEMISTRY

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PREFACE

This volume represents a desire on the part of the writer to place in the hands of his students a concise account of the development of the numerous theories of chemistry. It is his purpose to use it as a text-book, to be supplemented by lectures. And it is further hoped that the material presented may serve as a basis for more extended study. No claim is made for originality. It is an old, old story—many times told—gathered from innumerable and even forgotten sources, to which most cordial acknowledgments are here made for all borrowed facts and statements. The writer is likewise under many obligations to Miss Sarah P. Miller, Ph.D., Girls' High School, Philadelphia, for the skill and patience she has shown in condensing hundreds of pages of manuscript into the present compact form, and superintending the proof-reading and press work with the utmost fidelity and care.

THE THEORIES OF CHEMISTRY.

The Grecian philosophers were the first persons who undertook an explanation of the creation and destruction of nature. The chief aim of the pre-Socratic philosophy was to account for natural phenomena. Every individual on viewing nature and the phenomena of nature regarded that one thing as the original of all other things, which to him seemed to be the most remarkable. Thus, Thales considered water to be the protoype, because he knew that without it life was impossible. Pythagoras said numbers were the cause of all things, for the reason that on considering the movements of heavenly bodies in accordance with mathematical laws numbers seemed to him to be most important and impressed him most deeply. Heraclitus said fire was the cause of all things, and Anaximander declared it to be matter. In the opinion of Empedocles matter consisted of four elements: earth, air, fire and water.

Aristotle maintained that there was an ur-substance at the basis of all things. This ur-substance could not be annihilated—it made all things possible. It had potentiality, but it was not real or actual. It possessed four fundamental properties. It was warm, cold, moist and dry. The union of any two of these properties gave rise to one of the four elements of Empedocles. Thus, earth was dry plus cold; fire was dry plus warm; water was moist plus cold; and air was moist plus warm. Differences in the material world were thus ascribed to the properties inherent in matter. Aristotle thought

there was a fifth element, which he called ousia-ether. It penetrated everything.

These ideas of Aristotle and Empedocles are thought to have been borrowed from even earlier sources. In other words, there were men before them who entertained similar notions.

Alchemy added many substances to the list of elements (earth, air, fire, water and ousia-ether) previously mentioned, in order to account for the properties of the metals. Geber introduced sulphur and mercury into the list. These he considered the basis of the metals. This is the first attempt to explain differences in substances by assuming a peculiar composition. Albertus Magnus, Roger Bacon, Raymond Lully, Arnold Villanovanus and a host of alchemists accepted, in the main, this thought of Geber. Basil Valentine thought salt was an element. To the alchemist sulphur represented the properties of alterability, decomposability and combustibility. Mercury represented metallicity, which was the cause of metallic luster and malleability. Salt stood for the property that resisted fire.

During the age of alchemy, the first attempts were made to convert the base metals into gold or silver. The belief in the "transformation or transmutation of the metals" held a powerful charm and led the men of this period to labor incessantly, by every conceivable means, in order to attain this end.

Later Paracelsus declared that the three elements, sulphur, mercury and salt, were not only the ingredients

of metals but also of all bodies, animal and vegetable alike. Paracelsus viewed disease as a disturbance of the proper proportion and correct "make-up" of these elements; hence he strove to eliminate the disturbance by external means, and in so doing became the founder of the school of iatro-chemists. This school made two great mistakes. It attempted to account for all life processes by chemical means, and it set a too narrow limit upon the domain of chemistry.

The greatest of the iatro-chemists were Paracelsus, Libavius and van Helmont, all of whom believed in the transmutation of metals, by means of the philosopher's stone, and in the *elixir vitæ*. The latter objected to the idea of the earth being an element.

The man who bitterly opposed Aristotle's teachings, who placed chemistry upon a scientific basis and who freed it from the shackles of "gold-making" and "healing" and the old doctrines of the constitution of matter, was Robert Boyle (1626–1691). He taught that all compounds in nature were derived from an ur-substance; that the many differences existing in these compounds were due to the varying properties of the minutest particles of this ur-substance, and that the varying forms and sizes of these particles, their movements, their positions at rest and their positions relative one to the other exercised a very marked influence upon the differences existing in these bodies or compounds. "These minutest particles," said Boyle, "consisted of substances extremely difficult to decompose." They entered into and came out of the compounds without sustaining any alterations

or changes whatsoever; hence these minutest particles were elements in the sense of that term as understood to-day. According to Boyle, chemical union consisted in the attraction of these minutest particles (the corpuscula—the constituents) one to the other, and chemical decomposition occurred when one of the two constituents of a compound had a greater attraction, a greater affinity for a third than for the one with which it was combined.

Boyle knew that increase in weight followed combustion. He had verified this by heating lead in a closed retort, but he was so thoroughly imbued with the dominant ideas of his time, namely, that increase in weight was due to the interpenetration of fire matter (union with fire), that it was not possible for him to clearly comprehend the nature of the substance governing this increase in weight. Mark, that *Robert Boyle weighed.* He called attention in 1662 to facts regarding the elasticity of air, and asserted that the volume occupied by a given mass of gas under different pressures is inversely as the pressure.

Hooke (1635–1665), in England, observed that saltpeter when heated gave out something capable of supporting combustion. His experiments are recorded in a little pamphlet, entitled "Micrographia."

Mayow, another Englishman (1645–1679), said that the spirit of saltpeter and the *spiritus nitroaerus* of air were one and the same, and it was this spirit which combined with lead and iron when they burned in air.

These germs of the correct idea of combustion, introduced by Hooke and Mayow, were doomed to pass into oblivion; for a German named Becher (1635–82) was

actively promulgating the idea that the phenomena of combustion originated in a peculiar volatile escaping earth or kind of sulphur. He further taught that metals and minerals, in general, were derived from three elements: (1) a vitrifiable earth, (2) a volatile earth, and (3) an igneous principle. The teachings of Becher represent the first consistent theory of the constitution of compounds and of chemical action. Becher's third element —the igneous principle, in the hands of his pupil Stahl (1660–1734), became the central point of a very definite theory. Stahl named the igneous principle *phlogiston*, meaning combustible. He regarded phlogiston as the principle of inflammability—the fire matter which existed in combination with other bodies. Phlogiston, in the mind of Stahl, was a hypothetical element—a pure fire, fixed in all combustible bodies, and was to be distinguished from fire in action or in a state of liberty. He declared that all combustible bodies were composed of phlogiston and a non-combustible substance. Stahl was blind to the fact, noted by English chemists, that a metal after its burning had greater weight than before. His hypothesis or theory, the doctrine of phlogiston, was truly a step backward when looked upon in the light of the observations of Boyle, Hooke and Mayow, yet it held sway from 1720 to 1789, more than half a century. It must be remembered, however, that this theory led, through experimentation, to the discovery of many facts, and that it brought these facts under definite viewpoints. The interpretation of the experimental data served to correlate facts for which vague and enigmatical explanations had formerly been given. This theory, of which so much has been written and so much has been said, briefly stated is this: Combustion depends

upon some principle which is present in every substance. This principle, identical in all combustible substances, escapes during combustion. Phlogiston is the principle igneous or the principle combustible. In combustion, the phlogiston passes out as a flame, while the non-combustible portion of the body remains; hence, the term "dephlogisticated" corresponds to the present term "oxidized" and "phlogisticated" corresponds to the term "reduced." A metal lost its phlogiston, was "dephlogisticated," when it burned forming a "calx" [oxide]; this was a loss of potential energy. When a calx of a metal was reduced to the metal by another metal or by a combustible body like carbon, it was "phlogisticated"—an increase of potential energy. The conversion of phosphorus into its pentoxide and of the pentoxide back into phosphorus was adduced as evidence of the theory of phlogiston.

It must be granted that in the absence of more accurate experiments, the combustion phenomena could thus be explained with some degree of probability and apparent certainty. In this connection it is interesting to learn the ideas entertained by chemists, other than Becher and Stahl, concerning this igneous principle or phlogiston. Some identified it with light, with flame, with coloring matters (particularly prussian blue), with hydrogen, with the principle of levity or of negative weight, and the like.

Stahl, in the enthusiasm of his possession, strongly opposed the blending of chemistry with medicine, and earnestly warned all of his adherents and followers against the pursuit of those ancient alchemical "will-o'-the-wisps" (ignes fatui), such as the philosopher's stone, the elixir vitæ, and the other impossibles.

A galaxy of talented men upheld the theory of phlogiston. They were Neumann, Pott, Margraff, Eller, Black, Hoffman, Boerhaave, Bergmann, Cavendish, Priestley and Scheele, each an honest investigator, each unconsciously contributing to the ever-increasing fund of experimental proof, which eventually caused the downfall of the first chemical theory. Frederick Hoffman, while holding with Stahl that sulphur consisted of acid and phlogiston, that combustible bodies contained something which might be described as phlogiston; yet, thought it very probable that metal calces were produced, not by the subtraction of phlogiston, but by the combination of the metals with an acid material. That was coming very close to the present idea. It is interesting to observe that he used the term "with an acid material." Shortly after (1778), Lavoisier used the term "acidifying principle" for oxygen, and calcination for the union of metals (not only metals but also non-metals) with oxygen. And Boerhaave, while not directly attacking the doctrine of Stahl, doubted the assumption of the existence of a combustible principle and of an earthy substance in the metals. So, imperceptibly, the entering wedge was surely and definitely fixed, and when Priestley and Carl Scheele made oxygen known to the world the course of chemical events indeed became changed. Yet everyone is aware that there had been fore-shadowings of the correct explanation of combustion in Hooke's writings, in the observation of Mayow, and in Boyle's knowledge of the increase in weight upon calcination. These were only fore-shadowings, but there had been written that which was nearer the truth than any of these observations, namely, the contributions of one, Jean Rey, on the increase in weight of tin and lead

on calcination; first published at Bazas in 1630 and reprinted (1777), together with notes and various letters bearing on the subject, at Paris. Rey attributed the increase in weight of various metals on calcination, to the action of air, anticipating, to some extent, the work of Lavoisier, a century and a half later. A few quotations from the essays of Rey may be of interest. His style is quaint and lively, and withal most entertaining.

"Formal Response to the Question, Why Tin and Lead Increase in Weight when they are Calcined.

"Now I have made the preparations, nay, laid the foundations for my answer to the question of the sieur Brun, which is, that having placed two pounds six ounces of fine English tin in an iron vessel and heated it strongly on an open furnace for the space of six hours with continual agitation and without adding anything to it he recovered two pounds thirteen ounces of a white calx, which filled him at first with amazement and with a desire to know whence the seven ounces of surplus had come. And to increase the difficulty, I say that it is necessary to enquire not only whence these seven ounces have come, but besides them what has replaced the loss of weight which occurred necessarily from the increase of volume of the tin on its conversion into calx and from the loss of the vapours and exhalations which were given off. To this question then I respond and sustain proudly, resting on the foundations already laid, that this increase in weight comes from the air, which in the vessel has been rendered denser, heavier and in some measure adhesive

by the vehement and long-continued heat of the furnace, which air makes the calx (frequent agitation aiding) and becomes attached to the most minute particles, not otherwise than water makes heavier sand which you throw into it and agitate, by moistening it and adhering to the smallest of its grains. I fancy there are many who would have been alarmed by the sole mention of this response if I had given it at the beginning and who will not willingly receive it being as it were tamed and rendered tractable by the evident truth of the preceding essays. For those without doubt whose minds were preoccupied with the opinion that air was light would have rushed to oppose it. Why (they would have said) does not one extract cold from heat, white from black, light from darkness, since so much heaviness is extracted from air, a thing inherently light? And those who chanced to have bestowed their credence on the heaviness of air would not have been able to persuade themselves that it can ever increase weight, being balanced in itself. On this account I was constrained to show that air had weight, which was recognizable by other means than the balance, and that even with the latter a portion previously changed and made denser could manifest its weight. All this I have done as briefly as I found possible and without advancing anything not strictly germane to this matter, to elucidate which at all points it only remains for me to state and refute succinctly some opinions which others have held or might hold, and to resolve the objections which might be made to my answer.

"Whether Lead Increases in Weight as well as Tin.

"I should have ended were it not that the sieur Brun informs me in his letter that having noticed the augmentation of tin he made the same experiment with lead, which he found to diminish by one ounce in the pound, which sank him still deeper in doubt, having imagined that the same increase should be there found as with tin from the proximity of their nature and from the identity of the process of calcination. But to the experiment of the sieur Brun I oppose the experiments of Cardan, of Scaliger, and notably of Caesalpinus, already mentioned, who says it is worthy of astonishment that lead on calcination increases in weight by eight to ten pounds to the hundred. Shall I leave these persons in strife each to sustain his own experiment? I am too pacific; behold their reconciliation effected! Some lead is more pure than others, either because it comes so from the ores or because it has been previously melted. Those named above have found augmentation with the pure lead; the sieur Brun, a diminution with the other.

* * * * * * *

"Conclusion.

"Behold now this truth, whose brilliance strikes the eye, which I have drawn from the deepest dungeons of obscurity. This it is to which the path has been hitherto inaccessible. This it is which has distressed with toil so many learned men, who, wishing to know it, have striven to clear the difficulties which held it encircled. Cardan, Scaliger, Fachsius, Caesalpinus, Libavius, have

curiously sought it but never perceived it. Others may be on its quest, but vainly if they fail to follow the road which I first of all have made clear and royal; all others being but thorny footpaths and inextricable byways which lead never to the goal. The labor has been mine; may the profit be to the reader, and to God alone the glory."

The great battle, between modern chemistry and the believers in the doctrine of phlogiston, began in 1774. It reached its zenith during the years 1783–89. It did not close until 1794. The leader of the new school was Lavoisier.

Priestley discovered oxygen on the first day of August, 1774, by heating the red oxide of mercury. This new gas (oxygen), superior to ordinary air in supporting combustion, was named "dephlogisticated air" by its discoverer.

Priestley thought that the non-combustible part of our atmosphere was saturated with phlogiston, on the assumption that a gas was so much the better adapted for supporting combustion when it contained within itself a small quantity of phlogiston. Common air by drawing phlogiston from burning bodies became, as Lavoisier thought, phlogisticated air, and on that account exhibited no attraction for phlogiston; or in other words, no longer had the power of supporting combustion. The phlogiston, evolved in the burning of combustible bodies and in the calcination of metals, was supposed to unite with the atmosphere, or better with the dephlogisticated air contained therein, and the product thus produced was

the cause of the increased weight of the calces. Lemery, in 1700, advanced the idea that the air given off during the solution of metals in acids was their combustible constituent. Priestley, guided by the thought suggested by Cavendish—that metals in order to unite with acids must part with their phlogiston—boldly announced that inflammable air [hydrogen] was either identical with phlogiston or that it was very rich in that principle.

In 1781, Cavendish noticed that hydrogen and dephlogisticated air, when exploded in a closed vessel, in proportions sufficient to almost entirely phlogisticate the burnt air, produced pure water; further that water was formed when a mixture of air and inflammable air was exploded; and, in addition, that there was a reduction of one-fifth of the volume of the former noticeable. According to Cavendish, water consisted of phlogiston and dephlogisticated air; inflammable air, of hydrogen [or phlogiston] and water. The action of the dephlogisticated air upon inflammable air, when exploded with it, was to unite with its phlogiston and yield water, and consequently to set free the water in the inflammable air.

In 1788, Priestley offered the suggestion that water entered into the composition of fixed and other airs, in order to account for the formation of water when inflammable air and dephlogisticated air united. Inflammable air, he thought, might be the principle of alkalinity and dephlogisticated air the principle of acidity.

Scheele believed in the existence of phlogiston. While experimenting, to ascertain the nature of heat and fire, he discovered that measured quantities of common air, when kept in contact with certain substances, became incapable of supporting combustion. As the specific gravity of the air had not augmented the decrease in

bulk, Scheele concluded, could not be due, as at first conjectured, to the absorption of phlogiston, so that the atmosphere must consist of two distinct bodies, one of which, the residual air, he assumed to be incapable of combining with phlogiston, and the other, having a strong attraction for that substance, united with it, producing heat, which had penetrated through the walls of the vessel containing it; hence the diminution of the volume of air.

"Heat," Scheele said, "was decomposed by means of bodies which had a strong attraction for its phlogiston." Calces of gold, silver, etc., were reduced by the phlogiston in the heat and consequently the other constituent of heat, empyreal or fire air [oxygen], was liberated. Subsequently, when it became impossible to ignore the consideration of the increase in weight noticed in many substances after their combustion or calcination, Scheele so far modified his views as to pronounce fire air to be a compound containing, with very little phlogiston, a saline principle and water, which last gave to fire air the greater part of its weight. When fire air formed heat by combining with phlogiston it gave up its water to the materials it dephlogisticated, and thus it was that they were rendered heavier by ignition. It was the water that attached itself to the calces and made them heavier.

The foregoing statements briefly contain the views entertained by Cavendish, Priestley and Scheele, three of the most able chemists, and not only by them but by many others laboring in the field of chemistry at this time.

Lavoisier's experiments and deductions now claim the attention. In 1772, he found that sulphur and phos-

phorus increased in weight on burning, so he conceived a true idea of the nature of combustion before the real character of air was solved. In 1774, Lavoisier melted tin in a large, closed, air-tight flask, which he had previously weighed. When the tin became coated with a thin layer of oxide the apparatus was allowed to cool and was then reweighed. Its weight was the same as at first, but on opening the flask air rushed in and the weight of the flask and its contents was then greater. The tin, by calcination, had abstracted something from the air, and had not, as required by the theory of phlogiston, added anything to it. Further, Lavoisier carefully noted the relative increase in weight of the tin and decrease in weight of the enclosed air; so that in 1775 he published a paper entitled "The Principle which Unites with Metals during Calcination." In this paper he commented on the heating of the calces of metals with charcoal, and said that the original metal plus fixed air, or carbon dioxide, must be the product of a union of an elastic substance with charcoal. Priestley had shown him this elastic substance in 1774, when he heated mercuric oxide in Lavoisier's presence and described the properties of oxygen, the elastic fluid which was evolved on heating a calx of mercury.

Neither the science of chemistry nor yet a change in its objects can be said to have originated with Lavoisier. The methods he introduced to attain these objects, the ideas he put forth concerning the constitution of bodies, and the explanations he gave of various phenomena were new and gave a new aspect to the science.

Indeed, the mine of chemistry had yielded rich returns before Lavoisier came to labor in it. He merely availed himself of the old workings, and, extending them, opened

the main lode. Said Liebig, "Lavoisier discovered no new body, no new property, no natural phenomena previously unknown; but all the facts established by him were the necessary consequence of the labors of those who preceded him. His merit, his immortal glory, consisted in this, that he infused into the body of the science a new spirit; but all the members of that body were already in existence and rightly joined together."

In his first paper Lavoisier never once indicated that he doubted the existence of phlogiston, and as late as 1775 he spoke of it, but in the following year he did express his conviction that for the elucidation of certain phenomena one must ascribe to phlogiston other qualities than those assigned to it by Stahl.

A noticeable feature of Lavoisier's work was that he weighed. Boyle weighed, and Rey, and many others had used the balance. Cavendish had measured earth, air, fire and water. But, notwithstanding all this, weighing was not so universally resorted to until the time of Lavoisier. He weighed everything, and from 1789 the balance became an instrument which was in constant use by the chemist to test the steps in his experimentation, so that it is proper to say that the *quantitative era of chemistry* began with the work of Lavoisier.

In 1777, Lavoisier combated the assertion of Priestley (and this is the first time that he ever mentioned the name of the Manchester philosopher) that air is rendered irrespirable by becoming loaded with phlogiston, and he also demonstrated that ordinary air in which candles were burnt furnished about two-fifths of its volume of fixed air, and that pure or dephlogisticated air under the same conditions became almost completely transformed into that gas.

It was in 1778 that he broached the theory that dephlogisticated air [oxygen] was the universal acidifying or oxidizing principle, which by combination with charcoal, with sulphur, with nitrogen, with phosphorus, formed carbonic, vitriolic, nitric and phosphoric acids, and with metals yielded calces. All the phenomena of combustion were explicable by means of oxygen and without the supposition of the existence of phlogiston, of which there was absolutely no evidence. The anti-phlogistic theory was being gradually evolved, and in 1783, Lavoisier declared absolutely against the doctrine of Stahl. It was then that he determined to discover the nature of the product of the combustion of hydrogen. He had heard that Cavendish obtained water when he burned hydrogen. He repeated Cavendish's experiments, and likewise found that water contained hydrogen. He further found that on passing steam through a red-hot porcelain tube filled with iron wires that he obtained hydrogen. He also discovered that one volume of oxygen combined with 1.9 volume of hydrogen to form water.

Lavoisier had long been unable to hold the doctrine that the hydrogen evolved by metals in acids, was their phlogiston. This he believed could not be true, since the calces were heavier than the metals, and that hydrogen, though light, certainly had weight. He explained the production of hydrogen liberated during the solution of metals in acids by assuming that water was decomposed, its oxygen uniting with the metals while the hydrogen escaped. In the case of nitric acid, however, he said the oxygen was probably supplied by the acid. This last opinion was the clinching fact in Lavoisier's theory—the key to the overthrow of the doctrine of Stahl.

In 1789, Lavoisier's magnificent treatise on elementary chemistry appeared. The new chemical discoveries were described with great clearness and ability. The anti-phlogistic theory was set forth—demonstrating that during combustion there was a combination with oxygen. Oxygen was the universal acidifying or oxygenizing principle (he made the mistake, however, of laying too much stress upon oxygen as the acidifying principle, as shall be learned later). In addition, he deduced the great Law of the Indestructibility of Matter. He, too, disproved the idea of the elemental nature of heat, laid the foundation of modern chemistry and defined elements exactly.

One often wonders at this day what effect these statements of Lavoisier had upon the men of that period. Priestley wrote: "The doctrine of the decomposition of water being set aside, that of phlogiston, which in consequence of the late experiments on water has been almost universally abandoned, will much better stand its ground." From a recent reading of an old pamphlet published in 1798, in this country, entitled "A Sketch of the Revolutions in Chemistry," it may be added that the chemists of the United States, although favorably inclined to the French School, to the anti-phlogistic notions, yet maintained that until Priestley, was converted to the new notions they could not feel safe that the modern ideas (as they were then) were absolutely true, because of all those contending on this subject, Priestley stood pre-eminent as an experimenter.

Cavendish never abandoned his faith in phlogiston. Priestley, who emigrated to the United States and died there in 1804, corrected proofs on his death bed of a paper entitled "Phlogiston Established." He was the last of the believers and defenders of that faith.

Berthollet, while accepting the explanation of calcination and combustion, did not deem the acidifying principle essential.

In Germany, national prejudice naturally declared in favor of Stahl, but in 1792, after Klaproth performed Lavoisier's experiments before the Berlin Academy, he and other German chemists were convinced of the truth of Lavoisier's ideas, hence it may be said that the overthrow of the phlogiston theory in Germany occurred in 1792.

Conversion to the new ideas was not instantaneous by any means. It took time. Yet the fate of the Stahlian philosophy was sealed. Many tried to support it, but eventually Lavoisier's explanations came to be regarded as satisfactory in every respect and his anti-phlogistic theory was universally accepted as a new system of chemistry.

"It was the glory of Lavoisier," wrote Davy in 1814, "to lay the foundation of a sound logic in chemistry by showing that the existence of this principle (phlogiston) or other principles should not be assumed where they could not be detected and proved to exist."

From 1790 forward the chemists of the world gradually abandoned the idea of phlogiston. As a result of this, Lavoisier and his immediate associates in France turned their attention to the establishment of the new nomenclature, part of which is used to-day. In conclusion, it may be said that this work of Lavoisier completes what might be called "the second landmark in the history of the development of chemical theory." But do not forget what was written by Jean Rey, and bear

in mind that it required more than one hundred and fifty years to establish a correct explanation of the processes of oxidation and of respiration. Things of importance are often very long in reaching their fruition.

In point of time, the next most important advance made in theoretical chemistry (the next landmark) was the presentation of the chemical atomic theory by John Dalton. From the very earliest times philosophers believed in the atomic character of matter; but until Dalton took this subject into consideration there was no real, earnest attempt made to apply it to chemistry. Dalton never maintained that he was the author of the atomic theory. He was the first to explain the effects of chemical combination by a theory which has stood the test of time. It is often heard from physicists and from those who deal in speculative philosophy that the day of the atomic theory has passed. This is not true. The day of the chemical atomic theory is still with chemists.

"The observations of the earlier philosophers," Dalton said, "has led to the conclusion, which seems universally adopted, that all bodies of sensible magnitude, whether solid or liquid, are constituted of a vast number of extremely small particles." Dalton never grew weary of explaining that homogeneous, elastic fluids are constituted of small particles. In his book on meteorology he insisted on the separate existence of aqueous vapor from other constituents of the atmosphere. This was the first germ of his chemical atomic theory, since he viewed the gases as consisting of independent particles,

In tracing the development of Dalton's chemical atomic theory a few abstracts from his early paper will be given. Newton, as evidenced by the first of the quotations, furnished inspiration to Dalton.

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'Newton had demonstrated clearly in the 23rd proposition of Book II of the 'Principia' that an elastic fluid is constituted of small particles or atoms of matter which repel each other by a force increasing in proportion as their distance diminishes.

"That the particles of elastic fluids are of different sizes and weights under like circumstances of temperature and pressure having been once established, it became an object to determine the sizes and weights together with the relative number of atoms in a given volume. This led the way to the combinations of gases and to the number of atoms entering into such combinations. . . . Other bodies besides elastic fluids, namely, liquids and solids, were subject to investigation in consequence of their combining with elastic fluids. Thus a train of investigation was laid for determining the number and weight of all chemical elementary principles which enter into any sort of combination one with another.

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"In my last lecture," writes Dalton, "we endeavored to show that matter, though divisible in an extreme degree, is nevertheless not infinitely divisible—that there must be some point beyond which we cannot go in the division of matter. The existence of these ultimate

particles of matter can scarcely be doubted, though they are probably much too small ever to be exhibited by microscopic improvements.

"I have chosen the word 'atom' to signify these ultimate particles in preference to 'particle,' 'molecule' or any other diminutive term, because I conceive it is much more expressive; it includes in itself the notion of indivisibility, which the other terms do not. It may perhaps be said that I extend the application of it too far when I speak of compound atoms; for instance, I call an ultimate particle of carbonic acid a compound atom. Now, though this atom may be divided yet it ceases to become carbonic acid, being resolved by such division into charcoal and oxygen. Hence I conceive there is no inconsistency in speaking of compound atoms, and that my meaning cannot be misunderstood.

"It has been imagined by some philosophers that all matter, however unlike, is probably the same thing, and that the great variety of its appearance arises from certain powers communicated to it and from the variety of combinations and arrangements of which it is susceptible. From the notes I borrowed from Newton this does not appear to have been his idea. Neither is it mine. I should apprehend that there are a considerable number of what may properly be called elementary principles which never can be metamorphosed into one another by any power we can control. We ought, however, to avail ourselves of every means to reduce the number of bodies or principles of this appearance as much as possible; and after all we may not know what elements are absolutely indecomposable and what are refractory, because we do not apply the proper means for their reduction. We have already observed that all atoms

of the same kind, whether simple or compound, must necessarily be conceived to be alike in shape, weight, and every other particular.

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"In the investigations on the number and weights of the elementary principles constituting water, ammonia, and the various compounds of azote and oxygen, conclusions were derived principally from the facts and experience of others, without any additional facts of my own discovery that merit particular notice.

"The composition and decomposition of water had been ascertained by British and foreign chemists; that of ammonia, by Berthollet and several others. The compounds of azote and oxygen had been successively developed by Cavendish, Priestley, Davy and others. I may, however, observe that the nitrous compounds have occupied a great portion of my time and attention at different seasons.

"The simple and easy method of combining the least portion of oxygen with the greatest of nitrous gas, . . . was the result of my own investigation, and affords a convincing proof of the real nature of what is called nitrous acid, which is constituted of one atom of oxygen united to two of nitrous gas.

"From the preceding remarks it will be perceived that I advanced thus far in my theoretical progress without meeting with much obstruction. The way had been paved by others. But when I directed my views to the compounds of charcoal and oxygen, and charcoal and hydrogen, I found that all the commonly received doctrines were adverse to my proceeding and irreconcilable with my views.

"Mr. Tennant's experiments in the Phils. Transact., 1797, has shown the identity of diamond and charcoal in a chemical point of view; but the succeeding experiments of Guyton Morveau on the combustion of diamond supplanted the former in the judgment of a great part of our chemists; diamond was concluded to be a simple body and charcoal the oxide of diamond. Mr. Cruickshanks soon after discovered the gas called carbonic oxide. The doctrine of the compounds of charcoal, or rather diamond and oxygen, then stood thus:

	Parts.	
Diamond	18	
Oxygen	10	
	28	Charcoal
Oxygen	41	
	69	Carbonic Oxide
Oxygen	31	
	100	Carbonic Acid

"A very little reflection convinced me that the doctrine of charcoal being an oxide of diamond was highly improbable; and experience confirmed the truth of Lavoisier's conclusion that 28 parts charcoal plus 72 of oxygen constitute carbonic acid, also that carbonic oxide contained just half the oxygen that carbonic acid does, which indeed had been determined by Clement and Desormes, two French chemists, who had not, however, taken notice of this remarkable result."

* * * * * * *

In the last lecture of this course Dalton explained his singular and, as it turned out, altogether erroneous views respecting the chemical nature of chlorine, hydrochloric and hydrofluoric acids.

"Lecture 20, February 3, 1810.—Chemical Elements.

"When we consider the very important part which the two elementary atoms of hydrogen and oxygen seem to perform in the arrangement of chemical compounds we are inclined to wonder that no more than one compound of these two elements themselves should be found.

"Water, that most beneficial essential of all liquids, is formed of oxygen and hydrogen. Besides this one there is not a compound of these two elements generally known and recognized as such. It is singular if we have not somewhere a principle consisting of two atoms of oxygen and one of hydrogen or two of hydrogen and one of oxygen. The former of these ought to be an acid, conformably to what we observe in other similar cases; the latter ought to be a combustible gas. All the other common elements: azote, charcoal, sulphur and phosphorus, combine each one with two atoms of oxygen to form acids. Why should not hydrogen do the same? This question has been frequently put, but no satisfactory answer has been given. Upon comparing the results of experience and applying the theoretic views which I have been endeavoring to develop, it appears to me very probable at least that the acids denominated fluoric and muriatic, with derivatives, are constituted of the elements of hydrogen and oxygen, and are in reality the very

compounds of which we have just been hinting. I would not, however, be understood to mean that these views are the necessary result of the Atomic Theory, and that its truth or falsehood depends upon the determination of the question. From the want and imperfection of facts relating to these subjects nothing, perhaps, decisive can be yet advanced. I intend to point out such reasons and such facts as have induced me to adopt this opinion, and must leave it to others to judge how far they support the probabilities above mentioned."

* * * * * * *

Then Dalton gives short memoranda of the analytic and other grounds upon which he based his views. He concludes his course in the following words:

"I cannot conclude this course of lectures without expressing my high satisfaction with the general attention that has been given to the subjects under discussion, and with the indulgence which has been given me when adverse circumstances occurred. I shall always associate these grateful impressions with the recollection of the event. To those who feel highly interested themselves in the promotion and extension of science it is a peculiar satisfaction to meet with others of the same description. I shall now return to comparative retirement in order to prosecute the train of enquiry and investigation which I have briefly developed in the late lectures. The results, I am confident, will be found of importance, and will contribute to establish that beautiful and simple theory of chemical synthesis and analysis which I have adopted from a conviction of its application to the general phenomena of chemistry, and which will in due time, I am per-

suaded, be made the basis of all chemical reasoning respecting the absolute quantities and the proportions of all elementary principles, whether simple or compound.

"R. I., Feb. 3rd, 1810."

From these extracts it is clear that Dalton was a thorough-going atomist. He was deeply steeped in Newtonianism. For him the atoms, "hard, impenetrable, movable," had as actual an existence as if he had seen and handled them. He first saw in his mind's eye the atoms of oxygen, of azote and of watery vapor existing in the air. He drew them on paper, and tried to combine them so as to account for the homogeneous character of the atmosphere. In this endeavor he failed, and at once had recourse to another hypothesis, namely, that these atoms are not chemically combined, but that the particles of one gas act as vacua to those of another, thus accounting for the laws of diffusion which he had discovered some time previously. Then he concludes that the sizes of the atoms of different gases must be different, and "it became an object to determine their relative sizes and weights." And thus the foundation of the atomic theory was laid. But still the superstructure remained to be built up. Here again we can trace his further progress. Early in 1803, Dalton stated that the elements combine together in definite proportions to form compounds, for example: one atom of nitrogen with one of oxygen, and in no intermediate proportions. Dalton doubtless asked himself, "Why are these things so?" And the answer was not far to seek. If these gases are made up of small indivisible particles, and if chemical combination consists in the approximation of these particles—the clashing of the atoms, as it is now termed—

then it is clear that when two elementary gases, as oxygen and nitrogen, combine, the simplest form of the compound is that produced by one atom of the first coming into juxtaposition with one atom of the second gas. If any further combination is possible—and that possibility is not foretold by Dalton's theory, but is a matter to be decided by experiment—such a new combination can only be brought about by the juxtaposition of a second atom of one of the combining elements.

In Dalton's Laboratory Notebook for 1802–04, in the possession of the Manchester Society, there is the following entry on September 6th, 1803:

"Observations on the ultimate particles of bodies and their combinations."

And under this is written:

"CHARACTERS OF ELEMENTS.

⊙ Hydrogen	◑ Azote
○ Oxygen	● Carbone, pure charcoal
	⊕ Sulphur"

And a few pages farther on Dalton gives examples of his method of expressing the composition of chemical compounds:

"◑○◑ Nitrous Oxide	○⊙ Water
◑○ Nitrous Gas	◑⊙ Ammonia
○◑○ Nitric Acid	○● Gaseous Oxide of Carbon
○◑○ / ◑○ Nitrous Acid	○●○ Carbonic Acid
⊕○ Sulphurous Acid	○⊕○ Sulphuric Acid"

On another page of this notebook, with the date October 12, 1803, there is the following:

"New theory of the constitution of the ultimate atoms of bodies.

Characters		or thus
Ⓗ	Hydrogen	⊙
Ⓐ	Azote	◑
○	Oxygen	○
●	Carbone or charcoal	●
⊕	Sulphur	⊕
	Phosphorus	○"

And these are interesting as being the very first attempts to indicate by symbol the atomic construction of chemical substances.

In the chapter on "Chemical Synthesis" in Dalton's "New System" he explains the symbolic language which he uses:

"From the novelty as well as the importance of the ideas suggested . . . it is deemed expedient to give plates exhibiting the mode of combination in some of the more simple cases. . . . The elements or atoms of such bodies as are conceived at present to be simple are denoted by a small circle with some distinctive mark, and the combinations consist in the juxtaposition of two or more of these. When three or more particles of elastic fluids are combined together in one it is to be supposed that the particles of the same kind repel each other and therefore take their stations accordingly."

But the most important part of Dalton's theory remains to be considered; and it is this part which especially distinguishes it from all previous conceptions of the

constitution of matter. It was, "an enquiry into the relative weights of the ultimate particles of bodies—a subject," he adds, "as far as I know, entirely new. I have lately been prosecuting this enquiry with remarkable success." The weights of the atoms are different. The atom of oxygen is—according to Dalton, in the year 1803—rather more than five times heavier than the atom of hydrogen; that of nitrogen (azote) four times heavier, and so on; but every atom of the same element has the same unalterable weight.

The first published table of atomic weights was that appended to Dalton's "Memoir on the Absorption of Gases in Water," read before the Society on October 21, 1803. There is in Dalton's notebook an earlier table dated September 6th of that year, giving numbers differing somewhat from those of the printed table.

"TABLE OF ATOMIC WEIGHTS—SEPTEMBER 6, 1803.

Ultimate Atom of	Hydrogen	1.
" "	Oxygen	5.66
" "	Azote	4.
" "	Carbon (charcoal)	4.5
" "	Water	6.66
" "	Ammonia	5.
" "	Nitrous Gas	9.66
" "	Nitrous Oxide	13.66
" "	Nitric Acid	15.32
" "	Sulphur	17.
" "	Sulphurous Acid	22.66
" "	Sulphuric Acid	28.32
" "	Carbonic Acid	15.8
" "	Oxide of Carbon	10.2 "

It will be observed that no mention is here made of the two compounds of carbon and hydrogen, the names

and compositions of which are given in the table printed in the above-named memoir. Hence it is clear that Dalton had arrived at conclusions respecting the atomic weights of certain elements and of some of their compounds before the summer of 1804, when, according to his own statement, he carried out a further experimental inquiry into the composition of two compounds of carbon and hydrogen, namely, olefiant gas and light carburetted hydrogen, which led to results fully confirming the truth of his theory. These experiments showed that, as in the case of nitrous oxide and nitrous gas and in that of carbonic acid and the oxide of carbon, so, too, in the case of "carburetted hydrogen from stagnant water" and olefiant gas a simple multiple proportion holds good between the weights of the constituent elements; that is, the first of these gases contains just twice as much hydrogen to the same weight of carbon as the second (olefiant gas) does; and hence Dalton represented them by the symbols ⊙ ● ⊙ and ● ⊙ respectively. This conclusion was, however, not arrived at till 1804, and yet the numbers for the two hydrocarbons (6.3 and 5.3) appear in the table attached to a memoir of October, 1803. The explanation of this is that the volume of memoirs was not published till November, 1805, and that in the meantime Dalton made additions and alterations to the table. "It was in the summer of 1804," says Dalton, "that I collected at various times and in various places the inflammable gas (marsh gas) obtained from ponds." Those who wish to see how Dalton did this should visit the Manchester Town Hall and inspect the wonderful fresco by Madox Brown, where the process is clearly indicated.

The circular symbols used by Dalton are not employed

by chemists to-day. The elements are represented by the first letter or the first letter and one other letter of the name of the element (sometimes the modern, sometimes the Latin name); a small number placed below the symbol indicates the fact that more than one atom is present. Thus Dalton's two hydrides of carbon, at his time, would have been written CH_2 and CH, now they are written CH_4 and C_2H_4. This modern system was introduced by the Swedish chemist, Berzelius. Each symbol carries with it, a weight value. Thus H does not signify an indefinite weight of hydrogen but always one part by weight, and so for all the other elements, each having its own atomic weight understood. And so, too, for their compounds—the formula of a chemical compound not only indicates of what elements it is composed but also shows how much of each element is contained in it. The language of chemistry is, therefore, not merely qualitative but also quantitative.

It is a singular trait of Dalton's mind that he could not bring himself to adopt, or, if one may say so, even to understand this system of chemical nomenclature, apparently so simple and effectual. On the contrary, he considered it to be unscientific.

Dalton, to the end, adhered to the symbolic language which he introduced in 1802. That this was so is seen from a facsimile table of "Atomic Symbols" drawn up by him for a lecture delivered in the Manchester Mechanics' Institute on October 19, 1835. Writing to Graham so late as 1837, he says:

"Berzelius's symbols are horrifying; a young student in chemistry might as soon learn Hebrew as make himself acquainted with them. They appear like a chaos of atoms . . . and to equally perplex the adepts of science, to

discourage the learner, as well as to cloud the beauty and simplicity of the Atomic Theory."

Dalton's atomic hypothesis was brought prominently before the world of science, not by the author himself, but by an influential professor of chemistry, Dr. Thomas Thomson, of Glasgow. In August, 1804, Thomson spent some days with Dalton in Manchester, and as a result of their conversation Thomson became an ardent disciple of the new doctrine, which he taught at once publicly in his lectures and then introduced into his text-book published in 1807. In his "History of Chemistry" Thomson says: "Mr. Dalton informed me (1804) that the atomic theory first occurred to him during his investigation of olefiant gas and carburetted hydrogen gas, at that time imperfectly understood and the constitution of which was first developed by Mr. Dalton himself. . . . He found that if we reckon the carbon in each the same, then carburetted contains exactly twice as much hydrogen as olefiant gas. This determined him to state the ratios of these constituents in numbers, and to consider the olefiant gas a compound of one atom of carbon and one atom of hydrogen, and carburetted hydrogen of one atom of carbon and two atoms of hydrogen. The idea thus conceived was applied to carbonic oxide, water, ammonia and other substances, and numbers representing the atomic weights of oxygen, azote, etc., were deduced from the best analytical results which chemistry then possessed."

From what has been stated as to the genesis of Dalton's ideas, it is clear that this statement of Thomson is not quite exact. Dalton had formulated his theory and actually given numbers representing the relative weights of the atoms of certain of the elements and their com-

pounds in the early autumn of 1803, before he had investigated the composition of the two hydrides of carbon, which according to his own statement, he did not do until the summer of 1804.

Observe that throughout his work Dalton uses the term "relative weight." More than one hundred years ago the author of the atomic theory says nothing concerning the absolute weight of the atoms; and at present, the weights of atoms are "relative." No mortal eye has ever seen or ever will see an atom. Some notion of their probable size, however, can be gathered from the following: if a drop of water were to be magnified to the size of the earth the molecules of water would be larger than small shots but smaller than cricket balls.

How, then, did Dalton ascertain that the atoms of the different elements, being inconceivably minute, are not of the same weight, but that to each a definite number may be attached? In the first place, Dalton decided to compare the different atoms with hydrogen, taken as a unit, since hydrogen is the lightest known substance. It is then clear that this relation, existing between the weights of the atoms, must be obtained by calculation from the results of chemical analysis or synthesis of certain compounds of the elements. But on what principle was this calculation based? The principle or assumption adopted was that when only one compound of two elements is known to exist that compound consists of one atom of each element. That is the simplest conceivable arrangement, and the relative quantities with which these elements combine to form the compound are the least combining weights of the two elements.

It was found that 100 parts by weight of water contained $14\frac{1}{3}$ parts by weight of hydrogen and $85\frac{2}{3}$ parts

by weight of oxygen, or the elements were present in the proportion of 1:6; since Dalton's standard for atomic weight determinations was the hydrogen atom = 1, these numbers (1:6) were taken by him as representing the relative weights of the atoms of hydrogen and oxygen—water consisting of one of each.

In a similar way, the relative weights of the atoms of nitrogen and hydrogen were obtained. Ammonia gas is a compound of these two elements, and was supposed to consist of one atom of each of these. Analysis proved that it contains hydrogen and nitrogen in the proportion of 1:4.2 parts by weight. Hence this latter number is the atomic weight of nitrogen. Then, assuming this number for the atom of nitrogen, and knowing the composition of the two oxides of nitrogen, it is easy to calculate the atomic weight of oxygen in these two gases, and thus to show that oxygen enters into every combination with a definite fixed weight. This gives 4.9 as the relative weight of the atom of oxygen combined with nitrogen, against 6.0 when combined with hydrogen. The mean of these two numbers is nearly 5.5, a number adopted by Dalton in his first published table of atomic weights. In a similar manner the weight of the atom of carbon was found to be 4.5. The numbers obtained represent, then, the relative weights of the atoms and indicate the proportions by weight with which the elements combine to form definite chemical compounds.

Dalton subsequently made considerable changes in his table of atomic weights. This shows that, as time went on, he obtained other and more reliable data for his calculations. His first results were but rude approximations; his subsequent ones, though far from exact, were rather more in accord with present values. Indeed,

Dalton expressly states this: "It is not necessary to insist on the accuracy of all these compounds both in number and weight; the principle will be entered into more particularly hereafter, as far as respects individual results."

Nevertheless, in spite of his rough methods of experimentation, Dalton's results stand out as the greatest landmark of our science. His great achievement was that he was the first to introduce the idea of quantity into chemical language. It has been said, and with truth, that the atomic theory is almost as old as the hills; but no one before Dalton used the theory of atoms to explain chemical phenomena. To him is also due the glory of placing the science on a firm basis by showing that the weights of the atoms of the different elements are not identical but different. And, further, that combinations of these elements take place, if more than one compound be formed of the same elements, in simple arithmetical proportion.

Sir Humphrey Davy was much slower than Thomson to adopt Dalton's results. He was full of his discovery of the decomposition of the alkalies, and he writes to Dalton, in 1809, that while he is glad to hear his new views of the atomic system, yet he "doubts whether we have yet obtained any elements;" and in a letter to Dalton, dated May 25, 1810, Davy writes:

"I shall be sorry if you introduce into your rising system an hypothesis which cannot last concerning the alkaline metals." In 1811, he further objects: "I shall enter no further at present into an examination of the opinions, results and conclusions of my learned friend. I am, however, obliged to dissent from most of them and

to protest against the interpretations that he has been pleased to make of my experiments."

That Dalton was sanguine as to Davy's conversion appears from a letter addressed to Mr. Johns, in December, 1809. "Davy is coming very fast to my views on chemical subjects." And in 1826, he seems to have fully accepted his views, for in that year, Davy, then President of the Royal Society, spoke in the highest terms of Dalton's services to science when he presented the Royal Medal to him.

Soon after the volume of Dalton's "New System" was in the hands of chemists a discovery was made in France which, to the minds of almost all, came as a further striking proof of the truth of the Daltonian hypothesis. Strange to say, however, Dalton was about the only man to whose mind the experiments and conclusions of Gay-Lussac did not bring further confirmation of the atomic theory. Briefly stated Gay-Lussac's deductions were: that under similar circumstances of temperature and pressure, gases combine together in simple proportions by volume. Two volumes of hydrogen gas and one volume of oxygen gas unite together to form two volumes of water-gas. That Gay-Lussac's results were at once brought before Dalton's notice appears from a letter in the archives of the Manchester Society, from Dr. Thomas Thomson to Dalton, dated November 13, 1809: "The most important paper respecting your atomic theory is by Gay-Lussac. It is entirely favourable to it, and it is easy to see that Gay-Lussac admits it, though respect for Berthollet induces him to speak cautiously. His paper is on the combination of gases. He finds that all unite in equal bulks, or two bulks of one to one of another, or three bulks of one to one of another." Thom-

son then gives a list of the combining volumes of different elementary gases, as ascertained by Gay-Lussac, and adds that the French chemist declares that Dalton's experiments on this subject are incorrect.

Moreover, it appears from the following letter to his brother Jonathan, dated "12mo., 11th, 1809," that Dalton had in his possession the very volume which contained Gay-Lussac's celebrated memoir:

"About two months ago I received a very handsome present from Berthollet, sent me in return for mine sent him. It is 'Memoirs de la Société d'Arcueil,' being the most recent transactions of the Parisian chemists. It contains some very valuable papers. They speak very respectfully of my First Part." (Of his New System of Chemistry.)

In a similar strain Berzelius, who at once adopted the Daltonian theory, urges him in a letter dated from London, on October 13, 1812, to recognize the powerful corroboration of his system effected by the researches of Gay-Lussac. The words of the great Swedish chemist are as follows:

"Vous avez raison en ce que la théorie des proportions multiples est une mystère sans l'hypothèse atomistique, et, autant que j'ai pu m'apercevoir, tous les résultats gagnés jusqu'ici contribuent à justifier cette hypothèse. Je crois cependant qu'il y a des parties dans cette théorie, telle que la science vous la doit à présent, qui demandent à être un peu altérées. Cette partie, p. ex., qui vous nécessite de déclarer les expériences de Gay-Lussac sur les volumes des gases qui se combinent pour inexactes. J'aurais cru plutôt que ces éxperiences étaient la plus belle preuve de la probabilité de la théorie atomisque, et je vous avoue d'ailleurs que je ne croirai pas si aisément

Gay-Lussac en defaut, surtout dans une matière où il ne s'agit que de mésurer bien ou mal" (*sic*).

But Dalton remained obdurate, and as Angus Smith remarks, he does not appear to advantage in the contest in which he ventured to engage with Davy and Gay-Lussac. Dalton, it must be admitted, was not an exact experimental chemist. Although it may be urged that he was self-taught and began his work when the resources of the experimentalist were scanty and imperfect, yet, it is evident that there must have been some inherent deficiency, either in his mind or in his hands, which disqualified him for accuracy in experimentation. "Nature, it would seem, with wise frugality, averse to concentrate all intellectual excellencies in one mind, had destined Dalton exclusively for the lofty rank of a law-giver of chemical science."

The question has often been debated as to what extent Dalton supported Avogadro's law, namely, that the number of particles contained in a given volume is constant for all gases whether elementary or compound. Dalton's own words, contained in some manuscript notes for the lectures he delivered in Edinburgh and Glasgow, in 1807, leave no room for further question. The third lecture commences as follows: "Elastic fluids; mode of conceiving them. Are the particles alike in shape, weight, etc.? Query—are there the same number of particles of any elastic fluid in a given volume and under a given pressure? No! Azotic and oxygen gases mixed in equal measures give half the number of particles of nitrous gas, nearly in the same volume."

On the progress which atomic chemistry has made since Dalton's time, and especially in the last few years, it is not the province of this volume to dilate. Suffice it to

say, that the extraordinary complications in chemical combinations, which have been brought to light by modern research, all receive their explanation by the application of the principles of the Daltonian atomic theory. Without such a theory, modern chemistry would be a chaos; with it, order reigns supreme and every apparently contradictory and recondite discovery only marks out more distinctly the value and importance of Dalton's work.

In closing this sketch of Dalton's greatest discovery, it may be interesting to read the opinions of a famous Englishman and of a distinguished Frenchman on the life-work of the Manchester philosopher:

"The extreme simplicity," writes Sir John Herschel, "which characterizes the atomic theory, and which in itself is an indication, not unequivocal, of its elevated rank in the scale of physical truths, had the effect of causing it to be announced by Mr. Dalton in its most general terms, on the contemplation of a few instances, without passing through subordinate stages of painful inductive ascent by the intermedium of subordinate laws. Instances like this, where great, and indeed immeasurable, steps in our knowledge of nature are made at once, and almost without intellectual effort, are well calculated to raise our hopes of the future progress of science, and by pointing out the simplest and most obvious combinations—as those which are actually found to be most agreeable to the harmony of creation—to hold out the cheering prospect of difficulties diminishing as we advance, instead of thickening around us in increasing complexity."

Wurtz, in his "Histoire des Doctrines Chimiques," after indicating the work done by Wenzel and Richter, says:

"Mais l'interprétation théorique faisait encore défaut.

Elle découle des travaux d'un savant anglais qui a doté la science de la conception à la fois la plus profonde et la plus féconde parmi toutes celles qui ont surgi depuis Lavoisier. Au commencement de ce siècle la chimie était professée à Manchester par un homme qui joignait à un armour ardent de la science, cette noble fierté du savant sait préférer l'indépendance aux honneurs, et à une vaine popularité la glorei des travaux solides. Ce professeur est Dalton; son nom est un des plus grands de la chimie."

In the case of almost every great scientific discovery, many men's minds have been working in the same direction, and it often becomes a question of interest to discuss how far the acknowledged discoverer had been assisted or even anticipated by those who had gone before him. Such a discussion has been raised in this instance. Some have even asserted that Dalton was a plagiarist, and that the credit of the establishment of a chemical atomic theory belonged to others. This is not the place to discuss the question at length. Those who desire to make themselves fully acquainted with the facts and arguments may turn to the pages of either Henry or Angus Smith, where they will find the whole matter clearly and satisfactorily dealt with. It must suffice here to state that a careful consideration of all the circumstances has led to the conclusion, that Dalton arrived independently at his important results.

Others had expressed opinions and gathered facts to support these opinions, which approached the complete theory, but they certainly did not reach it. Mr. William Higgins, an Oxford man, in 1814, claimed to be the rightful owner of the atomic theory, by virtue of the statements contained in a volume published in 1789. It appears

certain that Dalton was unacquainted with Higgins' work until several years after he published his "New System," and thus the charge of plagiarism is fully disposed of. Indeed, no one who has appreciated Dalton's character could imagine that he would be guilty of such a proceeding. He was a man of original ideas, and paid little attention to the work of others, often to the extent of refusing to admit truths which were apparent to other minds. Still it might be that Higgins and others had the priority in the conception of the atomic theory and then in the history of science Dalton would have to take the second place. Such is, however, not the verdict of either contemporary or of later chemists all the world over.

Further, it may be asked, was Dalton alone in the discovery of the law relating to the definite combination of elements by weight, and of the law of multiple proportion?

It may truthfully be affirmed that Dalton developed these fundamental laws of our science, while ignorant of the fact that several others before him had had similar ideas in regard to chemical combination, and had formulated conclusions similar to his own but reached by entirely different paths. The work of Dalton is largely speculative—experimentally it is weak; the other scientists, who called attention to the definiteness of the combining power of elements and whose work antedated that of Dalton, were experimentalists, who did little philosophizing, but who recorded experiments which led to the same goal as that attained by John Dalton.

In 1777, Wenzel published a book entitled "Lehre von der Verwandschaft der Körper," in which the author describes "Decomposition by Double Transposition." The changes occurring were quantitatively determined, and this appears to be the first work of its kind. Considering the period in which this work was done, the results are really admirable. Wenzel confirmed, by his experiments, the theoretical ideas which had arisen: that whenever two neutral salts come together, double transposition takes place, and the salts which are formed are invariably neutral. He, also, explained this phenomenon. Suppose A and B to be the salts undergoing decomposition, and that A contained the base (*a*) and the acid (*b*), while B contained the base (*c*) and the acid (*d*). If the quantity of the base (*a*) in the salt A sufficed to completely neutralize the acid (*d*) in the other salt, B, conversely, the base (*c*) of the salt B would be sufficient for the complete neutralization of the acid (*b*) in the salt A.

$$Ca(NO_3)_2 + K_2SO_4 = 2KNO_3 + CaSO_4$$

The resulting salts were neutral, for the reasons that have just been given, namely, that there was sufficient nitric acid in this first salt to neutralize the base of the second salt when it was liberated, as there was also sufficient acid in the second salt to neutralize the base of the first salt upon its liberation.

Please note that while, to-day, this is so simple, so self-evident, at the time Wenzel began his work it was purely speculative. Wenzel confirmed his assertions by many additional analyses. He concluded from them that the various but definite quantities of different bases, required

for the saturation of a definite amount of one and the same acid, must be exactly in the same proportion as would be required to neutralize definite amounts of any other acid. The principle underlying the doctrine of equivalents is undoubtedly manifested in Wenzel's conclusions. His fate was that of so many, namely, that he was not recognized as one of the authorities of his day, and hence his investigations did not receive the attention and recognition they merited. Further, his results were compared with the analyses, faulty though they were, of the supposed authorities of that time, and as they did not harmonize therewith, they were pronounced erroneous and forgotten.

Some years later (1782) Bergmann observed that, when a metal was precipitated from the solutions of its salts by another metal, the metal in solution contained just enough oxygen to combine with the other metal and bring it into the form of an oxide, so that it would dissolve. If a strip of zinc is introduced into a copper sulphate solution, copper will be precipitated. In the judgment of Bergmann the copper was precipitated because it contained enough oxygen, so that when it came in contact with the zinc, its oxygen was sufficient to combine with the zinc, and the zinc oxide united with the SO_3 to form zinc sulphate. Here, again, is the idea of equivalents, and the idea of definiteness of combination. Unfortunately, Bergmann announced his observations in the language of the phlogistians, so that the explanations which he gave were wholly inadequate, difficult to understand, and the doctrine of definite ratios in combinations remained undiscovered.

But it remained for J. B. Richter, a German chemist, to review the work of Wenzel, and by his own experimenta-

tion to push forward these investigations; he brought them together in an exceedingly suggestive volume, entitled "Anfangsgründe der Stöchiometrie," published in 1792 to 1794. It contained the following declarations: First, "when two neutral compounds react upon one another, a transposition occurs, and the resulting products will always be neutral." That proposition had been demonstrated by Wenzel. The second principle announced by Richter read, "when, on the other hand, one of the two compounds reacting upon one another is not neutral then one of the products will not be neutral." Third, "it will be discovered, that upon determining the ratios of some neutral salts, it becomes possible, by simple equations, to calculate the composition of other neutral salts." Richter gave in tabular form the quantities by weight according to which the best known acids and bases unite with each other to form neutral salts. This, he called "the mass series or neutralization series;" 1000 parts by weight of sulphuric acid constituted the standard, to which all other members were referred. The numbers were found by comparing the quantity of any one base (A, for example) which was sufficient for the saturation of 1000 parts of sulphuric acid, and then calculating how much of another acid, B, the found quantity of A would neutralize, and from the quantity of B, was calculated the quantity of a base, G, which would be neutralized by that particular quantity of acid, and so on through the series.

In order to comprehend fully the importance of what Richter did, it is well to present a few examples from his work. With sulphuric acid as the basis and its value set at 1000, Richter proceeded to study calcium sulphate, and according to the results of his analysis of that body, there was present in it, 55.77 parts sulphuric acid (SO_3)

and 44.22 parts calcium oxide (CaO). He found the ratio number, as he termed it, by means of the proportion:

$$SO_3 : CaO :: SO_3 : CaO$$
$$55.77 : 44.22 :: 1000 : X$$
$$X = 793 \text{ (the value for CaO)}$$

The value for nitric acid followed from the value that had been obtained for the lime, 793, and from the analysis of calcium nitrate, which, according to Richter, contained 63.92 parts nitric acid and 36.07 parts lime.

$$CaO : N_2O_5 :: CaO : N_2O_5$$
$$36.07 : 63.92 :: 793 : X$$
$$X = 1405 \text{ (the value of nitric acid)}$$

The value for soda was determined from the nitric acid value (1405) and from the analysis of sodium nitrate, made by Richter, according to which it contains 62.05 parts nitric acid and 37.94 parts soda. The calculated soda value was 859. The value for hydrochloric acid was obtained from the soda value (859) and it proved to be 712. That for potassium was similarly calculated from the found value of hydrochloric acid and was discovered to be 1605. The value of sulphuric acid finally, if it had not already been known, might be calculated from this value of potassium (1605) and from the composition of potassium sulphate. It proved to be by actual experiment 1000.

A few of Richter's tables are submitted. It may appear, at first, that they have no bearing on the laws announced by John Dalton, but, upon investigation it becomes manifest that there is an intimate connection between them and the results of Dalton.

MASS OR NEUTRALIZATION SERIES FOR BASES AND ACIDS

Alumina	525	HF	427
Ammonia	609	CO_2	577
Magnesia	614	WO_3	700
Lime	793	HCl	712
Soda	859		
Beryllium oxide	1053		
Manganese oxide	1143		

The total value of calcium sulphate was 1793 (1000 for the sulphuric acid and 793 for the lime); to find the percentage amount of sulphuric acid in one molecule of calcium sulphate, the proportion would read:

Calcium sulphate : Sulphuric acid ::
1793 : 1000 :: 100 : X

Similarly, the quantity of lime in calcium sulphate could be calculated. Many more examples of this kind were given by Richter, but it is evident from these that he should be regarded as the founder of mathematical chemistry. His experiments demonstrated, beyond question, that there is a definiteness of combination on the part of the ultimate particles of matter; otherwise it would not be possible to have salts of definite composition formed by bringing together calculated amounts of base and acid.

The question has been asked why the observations of Richter were not known to the chemists of Germany, England and France. Why were they unknown to Dalton? The reason seems to be, that the whole subject was considered from a purely mathematical standpoint, and the men who were then laying the foundations of chemistry were averse to introducing mathematics into their subject.

Berthollet, who followed Lavoisier as the leader of the French School, published statements which were antagonistic to the Dalton doctrine. He argued that the affinities of elements one for another varied; and that this affinity, this force of attraction or attracting power, determined the question of what quantities should be present in the combination, so that there might not only be the ratio 1:1, but the ratio $1:1\frac{1}{3}$ or $1:1\frac{1}{2}$ and so forth. In short, the elements combine with one another in indefinite quantities by weight.

Proust, a fellow-countryman, took exception to Berthollet's declarations. By exact experiments he confirmed Dalton's statement: that the elements combine in definite quantities by weight. Proust also noticed that when two elements combine with one another in more than one proportion by weight, the second combination was also definite. This he observed before Dalton announced his law of multiple proportions. Proust failed, however, to observe that this second combination was a multiple of the first. In brief, he just missed the law of multiple proportions. He confirmed his observations by numerous analyses, but he did not make deductions, and the credit of having made the discovery of the law of multiple proportions belongs to Dalton.

The controversy between Berthollet and Proust began in 1799, and extended over a number of years. It was conducted in a perfectly friendly way, with the final result that Proust won. He showed that Berthollet had been analyzing the hydrates of bodies. These, on standing, gave up more or less moisture, and consequently the ratio between, for example, the oxygen of an oxide and its metal, varied from day to day—depending upon the water present.

Shortly after this, in 1805, Gay-Lussac, with Humboldt, contended that one volume of oxygen and two volumes of hydrogen united to form two volumes of water. This discovery has already been referred to (page 38) and was one which certainly could be looked upon as a confirmation of the law of Dalton. Gay-Lussac met with difficulties in his attempt to apply his observations to the theory of Dalton, owing in part to the very confusing ideas which were entertained concerning the atom of Dalton. However, he published his results in these words: "gases combine chemically according to definite volumes." This was in 1808. He made a careful study of this law alone and in conjunction with Humboldt, and said that in the union of hydrogen and a halogen, one volume of hydrogen gas and one volume of chlorine gas combine to form two volumes of the halogen hydride. Hence, the halogen hydride occupied the space previously occupied by its constituents. This was an important deduction for the chemical atomic theory. It was concluded that as hydrogen and chlorine united in the ratio of their combining weights, the ratio between the weights of equal volumes of these gases must be the same as that between the combining weights of these elementary gases, and that, consequently, according to Dalton, it could be assumed that the combining weight and the atomic weight were one and the same. The gas density would then be proportional to the atomic weight. Gay-Lussac and Humboldt were assuming that in equal volumes of different gases there were present an equal number of atoms—smallest particles. If 1000 atoms of hydrogen constituting one volume, united with 1000 atoms of chlorine, constituting one volume, there would result, according to these investigations, 1000 atoms of hydrogen chloride or

two volumes. One volume of hydrogen chloride would, therefore, contain only half as many particles—or atoms —as a like volume of the elementary gases, a conclusion which they saw contradicted the laws relative to the constant physical deportment of the gases, which laws had previously been discovered by them. To solve this contradiction required almost a half century of chemical investigation.

John Dalton, as previously noted, was not willing to accept any of these generalizations or deductions of the French School. Berzelius did accept them and used them in his magnificent work upon the atomic weights, to which reference will be made later.

In 1811, Avogadro announced a law, given on page 40, that under similar conditions of temperature and pressure, equal volumes of gases contain the same number of particles, which need not of necessity be *atoms*. It was probably Berzelius who suggested the term *atoms*.

This law, which seemed to offer an explanation of the difficulty which had been encountered by Gay-Lussac and others, did not meet with approval. There was apparently no need for it at that time, and it remained almost forgotten until 1850. The hypothesis of Avogadro is sometimes called the hypothesis of Ampère, since it was published by him, in 1814.

During the opening years of the nineteenth century (1800–1810) it became evident that the science of chemistry was, from that time on, to develop along several distinct paths. These paths are not divergent, rather are they parallel. It not infrequently happened that workers

in one were found among those actively concerned in the other lines of research. Discoveries made in one line were eagerly employed, wherever possible, in pursuing the work along other lines.

Many chemists became interested in *the atoms and in a determination of their relative weights*. It soon became apparent to them, as this work progressed, that new methods must be found by which they were to determine these weights. As a consequence of this necessity, new working methods were discovered and descriptions of these will be found in this discussion of atomic weight determinations.

Those engaged in the second line of inquiry sought to explain *the possible constitution of chemical compounds*. Many theories were proposed and a study of them is most interesting.

A number were led to search for *methods of experimentation whereby the constitution of chemical substances could be determined*, and this subject soon constituted itself a third line of research.

In 1801, still another line of inquiry was begun which led to the *amassing of theories and facts which finally culminated in the theory of electro-chemistry*. The theories formulated to explain solution, because of their many points of contact with those of electro-chemistry, are

included in this discussion. Electro-chemistry, the last subject to be considered, is thus placed because its greatest development has occurred during the closing years of the nineteenth century and the opening years of the present century.

Determinations of the Relative Weights of the Atoms.

Dalton's first table of atomic weights (1803) was both imperfect and incomplete. Thomas Thomson's estimations of atomic weights were even more faulty than Dalton's. In 1815, he wrote, "all the chemical elements are aggregations or condensations of one and the same primordial substance, because (1) gas densities are multiples of hydrogen, and (2) it appears that all atomic weights ought to be expressed in whole numbers, that is, multiples of the atomic weight of hydrogen, taken as a unit." This thought was not original with Thomson, although it appeared in his book. The author of it was an Englishman named Prout, who said that all atomic weights would be found to be multiples of unity.

In 1818, Meinecke, a German, announced the same thought. Naturally, discussions followed.

Berzelius and Turner proved Prout's hypothesis to be incorrect. Turner's table of atomic weights, however, was incomplete.

It was about this time that Berzelius began his memorable labors upon the atomic weight determinations. He had observed the efforts of Dalton and others, and was not pleased with the results obtained. He found occasion to question the purity of the materials used.

Further, he was not satisfied with the standard that had been selected by John Dalton and by his adherers, "because," he said, "hydrogen is an element with which comparatively few of the elements combine to form volatile compounds. Hydrogen unites directly with few of the elements. Most of the elements, however, combine with oxygen; and, therefore, it would be better for practical purposes to make *oxygen the unit of comparison*, and to determine the ratio between hydrogen and oxygen." With this suggestion of Berzelius and the previous suggestion of Dalton, before the minds of chemists, there arose a controversy which has continued through many years. To most people this controversy is a matter of very little interest; but to chemists, it is a matter of importance.

The determination of atomic weights forms a most important field in chemical endeavor, and deserves as much consideration as other factors, namely, the physical properties of the elements, etc. The atomic weights are among the constants of nature and should be studied both from the point of theory, as well as from that of practical utility.

One fact promulgated by John Dalton remains and, to-day, rises like Banquo's Ghost, not to disturb dreams, but to seriously harass wide-awake, thoughtful men. *It is that the weight of the hydrogen atom is one, and this element with its unit weight is, or should be, the standard of comparison in deducing the atomic weights of other elements.*

Among those who had entered this field of investigation was the mighty Nestor of the North—the honored and revered Berzelius. He made exhaustive analyses of numerous compounds, from which studies he drew definite conclusions, and gave the most complete list of atomic

weights ever published (see 5th volume of Berzelius' "Handbuch der Chemie").

Berzelius declared that one of the simplest methods of determining atomic weights consists in weighing all those bodies as gases which can be gasified and comparing their specific gravities with one another. However, this method is only applicable to very few bodies, and if applicable, the result, to be accurate, requires a high degree of skill in manipulation and very careful attention to a host of difficulties which must be overcome. One such difficulty is the securing of absolutely pure gases, another is the weighing of the gases, etc. And he adds, "*The commonest method to arrive at the atomic weights of elements is to combine them with oxygen, and to analyze the products with the greatest possible accuracy.* To render the found atomic weights comparable, choose one as the unit, and with it compare all the others—just as the specific gravity of a substance is compared with water taken as the unit of comparison. Dalton chooses *hydrogen*, because its atomic weight is the smallest of all the recorded values. I prefer to use the atom of *oxygen* as the standard because most compounds, with which chemistry is occupied, are oxides or compounds of oxides. I assign to the atom of oxygen the value 100."

Two masters in Israel, as may be seen, have given the units of comparison which in their respective judgments are best suited for the fixing of the atomic weights of the remaining elements. Dalton philosophized: "His inmost mental nature and all its outward manifestations were, in the language of the German metaphysicians, emphatically subjective. . . . In special or objective chemistry, he has left absolutely no sign of his presence; no great monograph on an individual body and its com-

pound; no memorable analysis of a substance deemed simple into yet simpler elements; no new element—no Neptune—added to the domain of chemistry." Professor Sedgwick wrote: "From the hour he came from his mother's womb, the God of Nature had laid his hand upon his head, and had ordained him for the ministration of high philosophy."

Berzelius experimented. He wrote, "I soon convinced myself by new experiments that Dalton's numbers were wanting in that accuracy which was requisite for the practical application of his theory. I perceived if the light which had risen upon the whole science was to be propagated, the atomic weights of as large a number of elements as possible, and above all of the most commonly occurring ones, must be determined with the greatest accuracy attainable. Without work of this kind, no day could follow the morning dawn. This being the most important point for chemical research. . . . I devoted myself to it with restless activity. After work, laboring for a period extending over ten years. . . . I was able to publish the atomic weights of about 2,000 simple and compound substances."

And of this experimenter, it has been written (H. Rose): "When a man, endowed with exceptional talents as an investigator, enriches every branch of his science with the most pregnant facts; distinguished himself equally in empirical and speculative research; grasps the whole subject in a philosophic spirit and arranges each detail systematically and clearly; gives out to the world a doctrinal system, critically sifted and put in as perfect a form as possible; and, lastly, when he proves himself a noble example of a practical and theoretical teacher, to a circle of pupils eager for knowledge, that man so fulfils

the highest demands of his science, that he will continue to shine forth as a brilliant model for ages to come."

That atomic weights were and are still needed, is evidenced by the attempts to prove or disprove Prout's hypothesis; and in the search for confirmations of the generalizations of Mendelejeff and Lothar Meyer. Grant them, then, theoretical importance. Have they any real practical value? When a chrome ore is purchased on a percentage basis—and one of the contracting parties uses in the calculations Cr = 52.2, and the other Cr = 52, a difference arises. It may, then, be safely asserted that the determination of atomic weights, has both a theoretical and a practical value. Such determinations should, therefore, be made and made with *all possible accuracy.*

Purity of material is the first essential in this work. It is also one of the most trying points in the problem. It demands that one should, by the most exacting methods, seek to eliminate every trace of extraneous substance.

The material being pure, the next step is its analysis.

"The accuracy of the analyses of Berzelius, being the admiration of the world, he was requested to make known his methods of procedure." Sebelien gives his answer in these words:

"Try to find that method in analysis, in which the accuracy of the result will depend, to the least extent, on the skill of the operating chemist; and when this method has been selected, then consider what unavoidable conditions are present which may cause errors in the result, and ascertain whether they will increase or diminish the same. Thereafter make another determination, in which exactly the opposite effects only can be produced. If the result remains the same, the determination was correct."

The analyses made, calculations follow. What shall be the unit of comparison? The hydrogen atom or the oxygen atom? This question has often been asked in the past; it is asked to-day. Down through the century which has elapsed since these standards were proposed, frequent changes have been made in their values, until at last with oxygen as the standard, it has received the value 16. This was believed to be its value compared with hydrogen = 1. A brilliant array of eminent men (none of whom stands out more prominently or deserves more praise than our fellow-countryman, Edward W. Morley) devoted their services to determining the exact ratio existing between hydrogen and oxygen. After years of experimentation that ratio is H:O :: 1:15.88; but if O = 16 then H = 1.0084. Whom does this affect? The theorist? Not at all—every analyst—every individual making chemical calculations is affected, or his work is; and it is largely because of the inconveniences to practical men, that in most recent times efforts have been made to establish a uniform basis. Three systems have come into use especially in the calculation of the results of organic bodies:

1.	H = 1	C = 12	O = 16
2.	H = $\left\{\begin{matrix}1.008\\.01\end{matrix}\right\}$	C = 12	O = 16
3.	H = 1	C = 11.91	O = 15.88

To what extent would the molecular weight of any substance, for example, oxalic acid or of cane sugar be affected by these values?

	System 1.	System 2.	System 3.
Oxalic acid:	126	126.06	125.10
	System 1.	System 2.	System 3.
Cane sugar:	342	342.22	339.60

The question is answered by these two examples. In this uncertainty as to what should be done, the German Chemical Society several years ago appointed a committee to examine into the question of a proper standard. That committee asked similar societies of other nations to unite with them in solving the problem. Three questions were propounded. Two of them will be given here:

1. Shall O = 16 be fixed as the future standard for the calculation of atomic weights?

2. Shall the atomic weights be given with so many decimals, that the last figure is certain within half a unit or what other procedure shall be adopted?

The first question alone is of interest in this connection. Forty-nine replies were received. Forty advocated the oxygen standard (O = 16); seven favored the hydrogen standard (H = 1), while two were undecided. This result was duly published and commented upon. The overwhelming vote for O = 16 was hoped to be final—it has not been. It was argued that teachers and technical men had not been given the opportunity to express their opinions. This was then done both through the committee of the German Chemical Society and through a committee of the Verein der deutschen Chemiker. While the questions were again being considered the German committee issued two atomic weight tables:

The International Table

$$O = 16 \text{ and } H = 1.008$$

and The Didactic Table

$$O = 15.88 \text{ and } H = 1$$

In the international table, about half of the recorded atomic weights are whole numbers or very close thereto,

while in the didactic table there are about ten expressed by whole numbers. To the practical man, to any one using these values frequently, the international table appeals strongly, because of its absence of decimals and consequent brevity. Since the result of the second vote has been published, there may be introduced here what appeared in the "Berichte" in December, 1901.

	For H=1	O=16
1. Great International At. Wt. Com.	7	40
2. Vote sent to Berlin, since first ballot	16	17
3. Through Volhard's Com	83	21
	106	78

Vereine for H..... 1
Vereine for O..... 4

Inasmuch as four of five "Vereine" had voted for O=16, it was thought best to adopt the "International Table of Atomic Weights." Perhaps abroad, more than in this country, there have arisen objections to this standard. Some of the arguments for the retention of the standard (H=1) may be given. It has the advantage of being the original Daltonian standard; it is the most natural basis for atomic weights, as the hydrogen atom is the lightest atom known and because hydrogen is the standard in gas densities and for valence. If the oxygen standard is adopted, then all vapor densities must be changed. An approximate unit, like 1.008, is meaningless. To teachers the hydrogen standard appeals, because it is easily intelligible to beginners, whereas the oxygen standard is somewhat difficult to explain. The physicists prefer the hydrogen standard because it approaches most nearly to an ideally perfect gas. "In the hydrogen thermometer, its nearly uniform rate of expansion is considered as well

as the fact that at low temperatures it is the last gas, except helium, to assume the liquid state. The graduation of the hydrogen thermometer is the ultimate standard of reference in all except thermometry . . . this question of harmony between different branches of science is one which needs to be seriously considered. . . ."

What can be said in favor of the other unit? Few elements can be directly compared with hydrogen; the latter has only been the theoretical standard, while the real basis in calculation has been oxygen. The familiar atomic weights are all in accord with this basis. The hydrogen scale is unfamiliar and its adoption in its modern form would oblige chemists to drop old values and learn the new.

Should not the opinions of the men who have devoted much of their time, energy and thought to the solution of this problem, have some weight? They of all others are alive to the existing difficulties—seen or unseen—arising from a selection of a uniform standard, and but two, Winkler and Mallet, of these men voted for the atom of H=1, as standard. Again, an atom of any other element could be chosen as the standard, for example, an atom of C=12. It is probable, from unpublished work, that hydrogen and oxygen would be found to possess values very close to 1 and to 16 were the C standard selected. At present, however, consensus of opinion has declared in favor of the oxygen standard—O=16 with H=1.0084.

During the first years of the nineteenth century the workers in this field met with many difficulties. The

chemical atomic theory had not become an established fact, and there were times when it seemed as if it would be set aside. Prout's hypothesis that all atomic weights would be found to be multiples of unity, met with very nearly general approval. As has been previously stated, Berzelius and Turner (about 1808) drew chemists away from this hypothesis and brought them back to the atomic theory. The work of Berzelius exerted a very great influence in more firmly establishing Dalton's hypothesis and in making his theory the basis of chemical science.

Another difficulty confronted those engaged in the work of determining the weight of the atoms—the uncertainty which existed concerning the formulas for substances. Berzelius, in particular, pointed out the unsatisfactory condition pertaining to the formula for water, from which was to be obtained the correct relation existing between the atomic weight of hydrogen and that of oxygen. From both the analysis and synthesis of water, there was invariably obtained two volumes of hydrogen and one of oxygen. The proportion of hydrogen to oxygen by weight had been proven to be 1:8—or the oxygen was eight times heavier than the hydrogen. In order to show these two facts, Berzelius wrote the formula for water HΘ, since he thought that oxygen was present in one to half of sixteen parts, or two of hydrogen to sixteen parts of oxygen; but this he could not prove. Other formulas were being used for water; frequently two or three formulas were employed for one and the same substance.

At this time Sir Humphrey Davy brought forward a new thought. Davy had been sceptical concerning Dalton's rights as the originator of the atomic theory,

and while he had later frankly recognized Dalton's service to the science of chemistry, he still refused to accept many of Dalton's conclusions. Davy was not ready to admit that Dalton had obtained atomic weights. He considered them to be the *proportion numbers of the elements.*

In 1808, Wollaston had raised the question as to whether these weights were "atomic weights" or were they not rather "*equivalent weights?*"

Gay-Lussac likewise rejected the idea of atomic weights; he thought that only *a ratio number was obtained.*

Berzelius believed the numbers obtained to be atomic weights. He worked alone. He appreciated the value of the discovery of Gay-Lussac's Law of Gas Volumes and, guided by this law, drew his conclusions concerning the union of elements; he found this law a valuable aid in determining the composition of many substances.

A glance at the table of atomic weights, published in 1818 by Berzelius, shows how reliable was his work when the values are compared with those of the present day. He used oxygen = 100 as the standard, and when his values for atomic weights are reduced to the basis of 0 = 16 ($H\Theta$), carbon = 12.12, sulphur = 32.3, iron = 109 (from the formula FeO_2).

The chemists of that time, like the chemists of to-day, were thinking over this point of the determination of the relative atomic weights, and were making all manner of suggestions, were executing all sorts of experiments in the hope of discovering some method which would be generally applicable.

The year 1819 brought two important discoveries, each in the field of physical chemistry. Both of these discoveries were valuable aids in the hands of Berzelius.

The first was a contribution of Dulong and Petit, in which they stated the law of atomic heats; the second discovery was made by Mitscherlich, whose work was embodied in the law of isomorphism.

Dulong and Petit found there was a simple relation between the combining weights and the physical properties of the elements that is, their specific heat or their capacity for heat in the solid state. *The atomic weights*, therefore, *were approximately inversely proportional to the specific heats, and as the result, the product of these two values was found to be nearly the same for all elements.* The atomic weight could be obtained, conversely, by dividing the constant (atomic heat) by the specific heat.

It was found necessary to alter the so-called combining weights of some of the elements in order that they might harmonize with this law. As might be expected, there were objections raised, but to-day the changes are willingly accepted.

The explanation of the fact in regard to the relation between combining weights and the physical properties of the elements is very simple. A few sentences from Lothar Meyer's work on theoretical chemistry will demonstrate this:

"As the specific heat is the amount of heat required to raise the unit weight of the substance from zero degrees to one degree centigrade, this product represents the amount of heat required to raise the equivalent weight by one degree centigrade. The weight of the given element, which is heated one degree centigrade, is termed the thermic equivalent weight. If we regard this as the atomic weight, then the product of the atomic weight into the specific heat is the atomic heat, that is, the amount of heat taken up by one atom. It is clear that

the atoms of the different elements have the same capacity for heat. The law may be simply expressed by saying that the atomic heats of all elements are approximately equal. This law can be applied without exception to all the malleable metals, to nearly all the brittle metals, to the majority of non-metals."

The specific heat of a substance, then, is the quantity of heat which increases its mass one degree in temperature.

Specific Heat	×	Atomic Weight	=	Atomic Heat
H	×	A	=	AH

Dulong and Petit determined the specific heats of copper, gold, iron, nickel, lead, bismuth, silicon, tin, zinc, cobalt and silver. They found the constant (AH) to be nearly 6.25.

Regnault determined the specific heat of a large number of elements, and obtained the constant 6.4.

Berzelius multiplied the specific heat of lithium (0.94) by its atomic weight (7—as he deduced it) and obtained the product 6.5. The same chemist multiplied the specific heat of sodium (0.293) by (23—the value that he found for its atomic weight) and the product was 6.7. The specific heat of phosphorus 0.17 multiplied by 30.9 gave 6.2 for a product. The mean of these constants was found to be 6.25. This method was a new and a decided aid in fixing the atomic values of the various elements. Berzelius altered, in consequence, a few of the results he had previously obtained.

The observations of Dulong and Petit in regard to the relation existing between atomic weights and specific heats being correct, there is provided a very simple means of determining the atomic weights of elements when once their specific heats are determined, because it has

been stated that if the constant 6.25 be divided by the specific heat, the atomic weight will result, so that this method gives a means of deciding which multiple of the combining number of an element is to be accepted as most probably expressing the atomic weight of that element. One illustration will suffice:

Weigh a piece of metallic tin, oxidize it with nitric acid, convert it into the oxide of tin, and re-weigh it, the increase in weight represents oxygen, by means of a proportion a number is obtained for the tin:

Weight of Oxygen : Weight of Tin : : Atomic Weight of Oxygen : X
16 : X

but if the proportion reads:

Weight of Oxygen : Weight of Tin : : 2 (Atomic Weight of Oxygen) : X
32 : X

then a different number results which is twice the first number. These results are the equivalent weights, but which is the atomic weight of the tin? It is at this point that the specific heat method is helpful. Weigh a quantity of tin (25 grams) heat that quantity to one hundred degrees centigrade, and when it has attained that temperature, suddenly throw it into water of a definite temperature. The heat of the tin passes to the water and raises the temperature of the water, and the increase in temperature bears a definite relation to the weight of the tin. It gives its specific heat. The constant 6.25, divided by that specific heat, will give either the value of X obtained in the first proportion or that of X of the second proportion, and the number which the specific heat gives is the most probable atomic weight.

The specific heats of forty-five solid elements have been directly determined and their atomic heats are nearly all 6.25. Six of the elements have had their specific heats determined directly in the solid state, and their atomic heats have proved to be 5.5. And five elements have had their specific heats determined in the solid state, and have given an atomic heat of nearly 6.25. The atomic heats of the gaseous elements are all very doubtful and apparently they are variable.

If fifty of the known elements yield this factor 6.25, it is evident that the law of Dulong and Petit is of some consequence; it cannot be the final method in determining the atomic weight of any element, but it can be of great assistance.

Attention, however, should be called to the exceptions to this law. They are beryllium, boron, carbon and silicon. These are important elements, but Pattison Muir thinks, in regard to beryllium, that too much value ought not be to given to its specific heat in the charts and tables, because the material that was used for its determination seems to have been impure.

He refers to the work of the Swedish chemists (Neilson and Pettersson) who conducted experiments on the specific heat of metallic beryllium containing known quantities of berryllium oxide, iron oxide and silica. They also determined the specific heat of pure berryllium oxide, and the specific heats of iron oxide and silica being known, they deducted values for these impurities from the specific heat of their mixture, and found the specific heat of beryllium was 0.407. The same chemists made a second series of determinations with a sample of the metal containing only about five per cent of beryllium and

ferric oxide, and obtained values for the specific heat varying from 0.397 to 0.505; hence these chemists concluded that the atomic weight of beryllium should be changed from 9.1 to 13.65. These experiments on beryllium are not conclusive. Will these impurities have the same specific heat in the mixture as they possess when alone?

All the more recent work on the atomic weight of beryllium, for example, the determination of it by one of the cryoscopic methods, gives 9.1 as its atomic weight. It is a bivalent metal and not trivalent, as it would be with the higher atomic weight.

Concerning the other three exceptions to the law of Dulong and Petit, Weber found the specific heats of carbon, boron and silicon increasing rapidly with rise of temperature, but at high temperatures the rate of increase was much smaller.

From the foregoing facts, it appears that the specific heat of every elementary atom is not a constant number but varies with the temperature, and that the relation between the variation of specific heat and that of temperature differs for each element. Hermann Kopp says of these three elements (boron, carbon and silicon):

"The atoms of these elements are probably built up of simpler parts, have a grained structure, and at high temperature, they are composed of a smaller number of these parts than they are at a lower temperature. Heat added at low temperatures is consumed in separating these atomic groups."

Muir adds: "the facts of spectroscopy seem to point to the existence of more complex structure in the non-metallic than in the metallic molecules; that allotropy

occurs distinctly among non-metals; that the molecules of the five metallic elements, whose vapor densities have been determined, are monatomic; that the atomic heat of tellurium, a metal like a non-metal, belonging to the group of oxygen, is 6; that of the less metallic selenium 5.8; that of the decidedly non-metal sulphur 5.5; and the typical non-metal, oxygen, not more than four; and, finally, that the molecular structures of oxygen, selenium and sulphur vapors are more complex than the structure of tellurium vapor." He concludes, "as silicon, carbon and boron are distinctly non-metallic, these facts lend support to the idea that part of the heat added to the carbon, the boron, and the silicon, at low temperatures is spent in separating the complex molecule groups into their constituent parts, rather than in separating the hypothetical complex atoms of the elements into smaller atoms." This is a matter which should not be lost sight of in considering the variations which have been discussed.

Mitscherlich's law of isomorphism, the second discovery made in 1819, also gave another means of determining the atomic weights. It was a less general and not so certain a means as the preceding discovery of Dulong and Petit.

This law was published in 1821, and in this form: "Equal number of atoms in a molecule, similarly combined, exhibit the same crystalline form; identity of crystalline form is independent of the chemical nature of the atoms, and is conditioned only by the number and configuration of the atoms." Accordingly, the quantities of the elements

occurring in isomorphous mixtures, would be to each other as their atomic weights. This fact makes it possible to establish a value for the atomic weight. There were two drawbacks to the law of Mitscherlich:

(1) Similar chemical bodies do not necessarily have identical crystalline forms, and
(2) Unlike chemical bodies may crystallize in identical forms.

The law could only be applied in cases where substances were *strictly isomorphous* (in cases where overgrowths occur). For example, if zinc sulphate will grow over copper sulphate crystals and the true form of the copper sulphate be retained then these two sulphates are strictly isomorphous. Isomorphism frequently occurs where there is no similarity in chemical composition; but overgrowths only take place where the composition is analogous.

Pattison Muir has written at some length, in order to show to what extent this rule of Mitscherlich is applicable.

Mitscherlich introduced the terms dimorphous, trimorphous, polymorphous. Many examples of the phenomena to which these terms were applied are now known. For example, calcium carbonate crystallizes in hexagonal form as calcspar and in rhombic form as arragonite.

The application of the law of Mitscherlich and of the law of Dulong and Petit to one example (determination of the atomic weight of iron) will suffice for illustration: The atomic weight of the element chromium is 52.4. The green oxide of chromium shows the same crystalline form as ferric oxide; these two oxides should, therefore, be represented by similar formulas. The atomic weight

of chromium being 52.4, and oxygen 16, the simplest formula that can be given to the green oxide of chromium is Cr_2O_3, and the formula for ferric oxide is, therefore, Fe_2O_3. If Fe_2O_3 is the correct formula for ferric oxide, it follows that two atoms of chromium are replaced, in one reacting weight of the oxide, by two atoms of iron; and the atomic weight of iron would be one-half the total weight of iron in the oxide—or 56. The specific heat of iron multiplied by 56 gives the constant 6.55, therefore, 56 is almost certainly the atomic weight of iron, and the formula for each oxide is correct.

The study of the crystalline form of substances has been an aid in the determinations of atomic weights. Before more extended and precise knowledge of the connections between crystalline form and chemical constitution is obtained, this method of determining the atomic weights of elements may only be applied tentatively and in a very few cases. The method is of use in suggesting possible lines of research. It is not improbable that the crystalline form of a substance is connected with the internal structure of the molecules.

This law has received considerable attention since 1819. Chemists and physicists, alike, have been anxious to make it applicable and trustworthy; so that it has been modified and remodified. It was made to read: "Isomorphous bodies have either similar chemical composition or the quantities of the elements in the compound vary but slightly."

Hermann Kopp, one of the earliest of the physical chemists, sought to simplify the existing chemical laws, and he modified this law of Mitscherlich to read, "isomorphism will exist only when bodies are capable of growing in a new solution."

Notwithstanding the attempts to modify this law, so as to accord with facts, it is of little assistance for the purpose for which it was suggested. It has been instrumental in determining the atomic weight of iron and of gallium.

Following the announcement of these two discoveries, Berzelius did not, at first, think that a revision of his atomic weights was necessary; but in 1826, he published a new table in which many of the values were halved—some were entirely changed. In this table Berzelius, for the first time, gives nitrogen and chlorine as simple substances.

The great difficulty still remained: What was the correct formula for water and the correct atomic weight for oxygen?

Gerhardt believed that H_2O was the correct formula for water, since it consisted of two volumes of hydrogen and one of oxygen, and eight times as much oxygen by weight as hydrogen; Berzelius, as has been seen, expressed the same thought by the formula $H\Theta$. Neither of these men could prove their speculations. In 1827, Dumas made a discovery which solved the problem. He discovered the method whereby the vapor density of substances could be determined. A definite quantity of a substance (in this case water) was converted into vapor, and this vapor compared with an equal volume of a standard, hydrogen, or air, or any other standard, but hydrogen was preferred. The weight of water vapor was thus found to be nine times heavier than one volume of hydrogen. The molecular weight of water would, therefore, be eighteen, and if in these eighteen parts by weight of water, there are two parts by weight of hydrogen, sixteen should represent the weight of the other constituent of water, namely, oxygen.

Dumas' method proved to be a valuable aid in determining certain atomic weights, but it was limited for two reasons: (1) all substances could not be converted into the vapor form, (2) chemists had not yet reached a proper understanding of the meaning of the law of Avogadro. When Avogadro's law was correctly interpreted, the second limitation was removed, and the method of Dumas became exceedingly helpful; it continued to be restricted, however, by the fact that not all substances could be vaporized.

Dumas in applying his method to atomic weight determinations was led into error. Berzelius retained his numbers. A comparison made of the atomic weights of Berzelius and of Dumas with those of the present day, prove that Berzelius was justified in considering his determinations correct.

About this time, Faraday had succeeded in decomposing water and several other compounds with the aid of the electric current, and he said "that equivalent amounts of hydrogen or metal were separated at the negative pole, and the corresponding quantities of oxygen or chlorine at the positive." In a determination of "electro-chemical equivalents" Faraday saw a sure secondary means for fixing doubtful atomic weights.

During the passing years there had been growing a confusion of ideas concerning the terms "equivalent," "atom," "molecule," but the time was not yet ripe for a clear cut exposition of these terms.

In 1831, Neumann published determinations of the specific heats of various solid compounds, chiefly of

naturally occurring minerals, and deduced the general statement "that the amounts of similar chemical compounds possess equal specific heats." It means this:—that the specific heat of free atoms is retained by them when they enter into chemical combination. Will this statement of Neumann be of any service? What are chemists trying to do? They (Berzelius, Dumas, Gerhardt, Laurent and others) are endeavoring to find better methods by which to determine the relative weights of the atoms of the various elements. Dumas' vapor density method was inadequate. There were exceptions to the specific heat method of Dulong and Petit.

If, then, Neumann could get the specific heat of a molecule (a), and, if the specific heat of one of the constituents (b) was known, the specific heat of the other constituent could be obtained by subtracting (b) from (a).

Neumann hoped that his observation might prove valuable in indirectly determining the atomic weights of certain elements, for example, chlorine— (1) the molecular or specific heats of metallic halides are: $RCl = 12.8$, $RCl_2 = 8.5$, $RBr = 13.9$, $RI = 17.4$, $RI_2 = 19.4$; (2) the atomic heat of each of the metals (R) is about 6.4; (3) the atomic heat of solid bromine and iodine is 6.6; (4) the chlorides, bromides and iodides are chemically analogous; (5) the molecular heats of analogous salts are nearly the same; it was, therefore, concluded that the atomic heat of solid chlorine was 6.4, this divided by the specific heat would give the atomic weight by an indirect method.

This method was applied to the determination of the atomic weights of fluorine, nitrogen, oxygen and a number of other elements, and gave results which were astonish-

ingly close to the numbers obtained for these elements by other methods, so that Neumann's method seemed satisfactory. But, as time rolled on, exceptions were found; so that the method was eventually abandoned.

Soon after the fourth decade of the nineteenth century began, Gerhardt and Laurent endeavored to bring about uniformity in the use of the chemical terms "equivalent" and "atomic weight." At this time it was a question of much concern what atomic weights should be ascribed to the elements, and what atomic (i.e., molecular) weights should be ascribed to compounds. Gerhardt's explanation was obscure. Laurent gave to his explanation greater clearness. Laurent based his deductions upon Avogadro's hypothesis and thus brought this law again before chemists. He, further, distinguished between "atoms" and "molecules," defining "*molecules* as the smallest particles of matter which could exist free or uncombined and which were absolutely necessary in order to bring about chemical action. *Atoms* were the smallest particles of an element which could occur in chemical combination." "Equivalents" were the quantities by which elements replaced one another. He further showed that the so-called "equivalent weights of elements" must be regarded as their "atomic weights," and the "equivalents of compounds" as their "molecular weights."

This work of Gerhardt and Laurent did not find immediate acceptance with chemists. Stronger proof was required that atomic weights should be applied to elements and molecular weights to compounds, than that given by these two chemists.

Gerhardt was using H_2O as the formula for water, which coincided in principle with the formula used by Berzelius, and with the deductions made and based upon Dumas' vapor density of water; but other chemists were using different formulas. It was during the fifth decade of the nineteenth century, that chemists most keenly appreciated the fact that they were using formulas which scarcely expressed the truth. The confusion arising from the use of different formulas for one and the same substance became very great.

How, then, could the atomic weights obtained be correct? Surely, this matter required speedy settlement, and it came in 1858.

It was in 1811, that a man named Avogadro, a physicist, made a statement frequently referred to in this text which was, "that in equal volumes of all bodies in the gaseous state there is an equal number of particles." It was Berzelius, who, after some experimental study and reflection upon this statement, wrote the proposition of Avogadro to read as follows: "that in equal volumes of bodies in the gaseous state there is contained an equal number of atoms."

The confusion which prevailed in the use of formulas and the desire to find some sure and common ground upon which to stand in this matter, led, in 1860, to a congress of the chemists and physicists of Europe. This congress was held at Carlsruhe. It was called on the part of the chemists of Europe at a time when the people of the United States were preparing to enter upon one of the most critical periods in the history of America. More than one hundred of those who had been invited accepted and appeared at Carlsruhe. Many of the chieftains of that time were missing, others after a brief stay departed.

However, it may be said that in the years which have since passed, there has never been a more brilliant gathering of chemists anywhere in the world.

During the congress, side issues so filled the days that the main subject for discussion was never reached.

There was, however, one address delivered by an Italian, named Cannizzaro, which appealed to every one present. Dumas had delivered a lengthy address, in which he developed the thought that chemistry consisted of two distinct sciences—the inorganic and the organic. This address was followed by an impromptu speech by Cannizzaro. He emphasized the fact that while organic chemistry had grown marvelously, and while it had been using other atomic weights and had been following other rules than those which were applied in inorganic chemistry, yet the science of chemistry was unitary in its character.

It is needless to say that Cannizzaro won the sympathy of the entire audience, which was expressed in the addresses later delivered by Hermann Kopp and Otto Erdmann, who said, among other things, that chemists must seek to bring together facts that have been observed in their discoveries and to unite them in one common plan.

This was in 1860. Lothar Meyer was present at that gathering. He was at Carlsruhe as a young man, and he wrote that he went from this congress in a very unhappy frame of mind. By the merest accident, however, there fell into his hands a letter which Cannizzaro, in 1858, had written to Professor Lucca. In this letter, Cannizzaro undertook to set forth the methods by which he successfully proved to his students the correctness and the great importance of the law of Avogadro, which had been enunciated early in 1811. Lothar Meyer

perused this letter on his way home from this congress, the scales fell from his eyes and he saw more clearly than he had ever seen before, how, by following the theory of Avogadro, with the modifications put upon it by Cannizzaro, it was possible for chemists to arrive at definite conclusions concerning molecular formulas. The formula established, the correct atomic weights of the constituent elements might then be determined.

That letter of Cannizzaro has since been published in Italian and, later, at the instance of Meyer, it was translated by one of his Italian students. It has been annotated and given out as one of the classics of the exact sciences in the series published by Ostwald. This book should be read because it is not only instructive but exceedingly helpful.

Cannizzaro insisted that the generalization of Avogadro, "equal volumes of gases contain an equal number of molecules," afforded a direct method of determining the relative weights of the molecules of many elements and compounds, without any knowledge of the compositions, or the reactions, of these molecules. "All that need be done," Cannizzaro said, "is to determine the densities of the substances in the gaseous state, and express the experimental results in terms of the standard element, which is hydrogen."

Avogadro had taken the molecular weight of hydrogen as unity. Cannizzaro said, "Instead of taking for your unit the weight of an entire molecule of hydrogen, take rather the half of this weight, that is to say, the quantity of hydrogen contained in the molecule of hydrochloric acid." This change of units brought home to chemists the principle they had been seeking for half a century; it put into their hands the knowledge they required and had overlooked. The following table of relative

densities of gaseous elements and compounds, and molecular weights of these substances, is taken from Cannizzaro's memoir published in 1858.

Name of substance.	Densities or weights of a gaseous volume, referred to the weight of a volume of hydrogen = 1; or molecular weights referred to the weight of a molecule of hydrogen as unity.	Densities referred to that of hydrogen taken as 2; or molecular weights referred to the weight of a semi-molecule of hydrogen as unity.
Hydrogen	1	2
Ordinary oxygen	16	32
Electrified oxygen	64	128
Sulphur under 1000°	96	192
Sulphur over 1000°	32	64
Chlorine	35.5	71
Bromine	80	160
Arsenic	150	300
Mercury	100	200
Water	9	18
Hydrochloric acid	18.25	36.5
Acetic acid	30	60

Since 1858, the determination of the molecular weight of homogeneous gaseous, or gasifiable substances has consisted in determining the density of that substance in the state of a gas. The result gives the number of times heavier a volume of that gas is than an equal volume of hydrogen, referred to the weight of a molecule of hydrogen = 2, or referred to the weight of a semi-molecule of hydrogen = unity.

Cannizzaro taught chemists how to express the compositions of molecules. He said, "If the substance cannot be decomposed, it is necessary to conclude that the molecules of it consist of one substance throughout. If the substance is a compound it is analysed, and the constant weight-relations of its constituents determined. The molecular weight is then divided into parts proportional

to the relative weights of the components, the quantities of the elements thus obtained in the molecule of the compound, are referred to the same unit as is used for the expression of all molecular weights." Cannizzaro illustrated this statement by a table of which the following is a portion:

Name of substance.	Weight of a volume, or molecular weight referred to the weight of a semi-molecule of hydrogen as unity.	Weights of the constitution of a volume, or a molecule, the sum being referred to the weight of a semi-molecule of hydrogen as unity.
Hydrogen.....	2	2
Ordinary oxygen...	32	32
Phosphorus.....	124	124
Hydrochloric acid..	36.5	35.5 chlorine + 1 hydrogen
Water.....	18	16 oxygen + 2 hydrogen
Calomel.....	235.5	35.5 chlorine + 200 mercury
Corrosive sublimate	271	71 chlorine + 200 mercury
Carbon monoxide..	28	16 oxygen + 12 carbon
Carbonic acid.....	44	32 oxygen + 12 carbon
Alcohol.....	46	6 hydrogen + 16 oxygen + 24 carbon
Ether.....	74	10 hydrogen + 16 oxygen + 48 carbon

Tables similar to this were arranged by Cannizzaro for several compounds of the same element. His table for several of the compounds of chlorine follows:

Name of compound containing chlorine.	Weights of chlorine in the molecules referred to the weight of a semi-molecule of hydrogen as unity.
Hydrochloric acid.....	35.5 = 35.5
Chlorine.....	71 = 35.5 × 2
Mercuric chloride.....	71 = 35.5 × 2
Arsenious chloride.....	106.5 = 35.5 × 3
Stannous chloride.....	71 = 35.5 × 2
Stannic chloride.....	142 = 35.5 × 4
etc., etc.....	... = 35.5 × N

Atomic weight of chlorine = 35.5

Cannizzaro's Law of Atoms.

Referring to this table and others like it, Cannizzaro said, "By comparing the different quantities of one and the same element, which are contained either in the molecule of the free element, or in the molecules of its compounds, the following law stands out in relief: The different weights of one and the same element contained in the various molecules are always whole multiples of one quantity, which is justly called the atom, because it invariably enters the compounds without division."

The application of the hypothesis of Avogadro to facts established by experiment concerning the volume-relations of various elements and compounds, led back to the conception of the atom.

The term *atom* is now applied to each of those smallest fractions of a molecule which are produced and again combined when molecules interact.

The weight of hydrogen in a molecule of hydrochloric acid gas is taken as unity, and it was agreed to call this the atomic weight of hydrogen. Then the weight of hydrogen in a molecule of that element is twice unity—in other words, the molecular weight of hydrogen is 2.

It is very essential that the student should understand clearly the meaning of the assertion that the molecular weight of hydrogen is 2. A certain volume of hydrochloric acid gas contains one part by weight (say, one gram) of hydrogen; an equal volume of hydrogen gas contains twice as much (two grams) hydrogen. Equal volumes contain (by hypothesis) an equal number of molecules; therefore, a molecule of hydrogen weighs twice as much as the hydrogen in a molecule of hydrochloric acid gas, that is, twice as much as the unit weight, twice

as much as the atomic weight, of hydrogen; in other words, the molecular weight of hydrogen is 2.

The Molecule and the Atom.

It was now made possible to form a clear notion of the expressions, *molecule of a homogeneous gas, and an atom of an element.* Avogadro said that the molecules of a gas are "the particles which are at such a distance from each other that they cannot exercise their usual action." In more recent times, Clerk Maxwell thus describes the molecule of a gas: "A gaseous molecule is that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of or agitation of the gas." The molecule of a substance is sometimes described as the smallest mass of it which exhibits the properties which are characteristic of that substance. This description is often stated more briefly thus: a *molecule* is the smallest mass of a substance which can exist in the free state.

The student must think of a gas as composed of a vast number of exceedingly minute particles, each of which has the properties which mark off the gas from all other substances; and consider these particles as moving about, sometimes colliding, sometimes traveling freely, but not breaking up (under ordinary conditions) into portions. The possibility of the occurrence of collisions between molecules of different gases must also be pictured. These collisions entail the shattering of molecules into parts; the student must see these parts—these atoms, rearranging themselves and forming new molecules. The *atom* of an element is the smallest weight of it which enters

into the composition of various molecules, referred to the smallest weight of hydrogen, as unity, which takes part in the formation of molecules.

The term *molecule* is applied to elements and compounds; the term *atom* is applied only to elements. The molecule is generally conceived to be a collocation of atoms; although there are cases where the molecule and the atom of an element are identical. The atom is the ultimate particle wherewith the chemist is concerned at present. Chemistry neither asserts nor denies the possibility of dividing the atom; it affirms only that if an atom were to be divided, the properties of the parts would not differ from those of the whole.

The hypothesis of Avogadro does not make any assertions regarding the relative sizes of molecules.

Order was thus brought out of chaos by Cannizzaro's interpretation of Avogadro's hypothesis. Chemists now possessed a means whereby formulas for chemical substances might be fixed; and from which the weights of the constituent atoms might be deduced.

Several theories had been proposed, before 1860, to explain chemical constitution. These theories, to some extent at least, prevented scientists from accepting Cannizzaro's explanation of Avogadro's hypothesis. Meyer, in his "Modern Theories of Chemistry," remarks of these theories: "they came into shape slowly, and were adopted slowly." In discussing Gerhardt's theory of types, Meyer comments on the fact that in the four volumes of his "Treatise on Organic Chemistry," Gerhardt confines his description of the type theory to not over one hundred pages at the close of the last volume, and does not use the theory in elucidating the constitution of a single compound. Gerhardt was ques-

tioned on this subject and confessed to a fear that his book would not be purchased if he had done otherwise. Meyer adds: "It is well for chemists, if this is really the condition of affairs, to turn away from further discussion of these various theories, and return to the determination of atomic weights; to make such investigations as will enable them to deduce correct formulas for the compounds being used, and to refer to the future, the arrangement of these formulas in accordance with the light which may later be discovered."

Half a century after the promulgation of Avogadro's hypothesis, the rapid development of organic chemistry, the knowledge of the density of gases, made necessary the logical and universal application of this hypothesis.

Clausius, further, recognized the necessity for this hypothesis on purely theoretical grounds arising from the mechanical theory of heat. Avogadro adhered to the doctrine of the material nature of heat, and, therefore, explained the expansion of gases by the repulsion exerted between the layers of heat surrounding the individual molecules. The hypothesis offers no means of explaining why the expansive force and its changes with the temperature, and with the change of volume, should be the same for all gases merely under these conditions. But it appears to be the only possible assumption if certain general considerations are taken into account.

By the aid of Maxwell, the relative frequency of any one of the many possible values of molecular velocity can be calculated. This calculation proves that in a mixture of several gases, the probability of a value for the energy of the molecules of a particular gas is just as great as for the molecules of any other gas. In a mixture of several gases, the molecules of one gas may possess double,

treble, half or third the energy of the others, but, the number of molecules in equal volumes of different gases must, according to the law of probabilities, be equal under similar conditions of temperature and pressure. In this way Avogadro's hypothesis attains to the same degree of probability which the kinetic theory of gases has attained. Avogadro's hypothesis must remain indispensable, whatever views should be held regarding the nature of the gaseous state. Important objections have never been raised to this hypothesis; whenever it has been discussed, the question has been merely concerning the convenience of explaining the hypothesis—its correctness has never been disputed.

The study of chemical reactions for the determination of the molecular weights, without the aid of Avogadro's hypothesis, is very deceptive and thoroughly inadequate as has been seen from the fact that molecular formulas and their corresponding molecular weights determined prior to the correct explanation of this hypothesis were universally regarded as unsatisfactory.

It is not possible to determine the absolute magnitude of the molecular weights by means of the hypothesis, but the relative magnitudes of the molecular weights of all bodies, the density of which in the gaseous state has been measured, may be determined, and the molecular weights are proportionate to the densities.

The chemists, who have exploited this hypothesis, agree that the weight of a molecule of hydrogen, which according to a previous statement contains at least two atoms, shall be represented as equal to two, but as Avogadro took the molecule and not the atom as unity, the numbers at present used for the molecular weights are double those he proposed.

This hypothesis in the form which it assumed after its modification and development by Cannizzaro, remains to-day and serves, as has been indicated, as the means for the deduction of molecular and atomic weights.

In concluding the subject of atomic weight determinations, certain more recent considerations must be added. Prout's hypothesis, previously referred to, according to which the atomic weights of all elements were to be regarded as simple multiples of the atomic weight of hydrogen, served for a long time to stir up strife and threatened the rational development of the atomic theory; that such a catastrophe did not occur is owing to the labors of the most eminent chemists of that time.

During recent years, Prout's hypothesis has again received attention. Döbereiner, L. Gmelin, Pettenkofer, Dumas, Odling and others observed that chemically analogous elements had atomic weights very nearly similar or which differed from each other by a definite increment. This fact gave rise to much speculation. Recently, an attempt has been made to systematically classify the elements in such a manner, that the connection between the natures of elements and their atomic weights would be apparent.

In 1864, Newlands and, a little later, Lothar Meyer, in Germany, independently *arranged a number of the elements according to the magnitudes of their atomic weights*, and observed that while those following each other showed no great similarity in properties, yet, after the lapse of a certain "period" the chemical and physical behavior of the elements repeated the behavior of those in the

preceding period. The elements resembling each other were placed in "*groups*" or "*natural families.*" The "*periods*" contain the elements having atomic weights between those of two adjacent elements in a "*group.*"

After 1869, these beginnings were extended and perfected by Mendelejeff and Lothar Meyer. At this time there existed greater accuracy in the atomic weights. Mendelejeff attempted to classify *all* of the elements according to the magnitude of their atomic weights. He showed that elements which were chemically similar (in *groups or families*) followed one another in regular periods. Elements were thus brought together in a "natural system," much, however, was arbitrary because of inaccuracy of the atomic numbers. The fundamental idea developed by these investigations, namely, "that the elements arrange themselves on the one hand into periods, and on the other into natural families, and that all their properties are periodic functions of their atomic weights," has been strengthened by further investigations.

By thus systematizing the elements it has been possible to make certain deductions, for example, definite values could be assigned to elements whose atomic weights were uncertain, since every element has a place of its own in the system; and as a consequence of this fact the atomic weight of molybdenum was corrected. Again, there were gaps in the system. Some of these have been filled by newly discovered elements, and these elements were predicted together with their approximate atomic weights and some of their properties, for example, germanium, scandium, etc.

One result of this classification was to demonstrate the fact that physical and chemical properties of all

elements show a periodic dependence upon their atomic weights. The discovery of the cause of this is yet to be made. Some of the scientists have returned to the idea of a simpler element for each group—a reappearance of Prout's hypothesis.

Crookes has again brought up this subject. After making observations on the phosphorescence spectra of the yttrium earths, he claims that elements are not simple substances but are to be considered as compounds

Periods	—	Group 1. RH R_2O	Group 2. RH_2 $RO(R_2O_2)$	Group 3. RH_3 R_2O_3	Group 4. RH_4 $RO_2(R_2O_4)$	Group 5. RH_3 R_2O_5	Group 6. RH_2 $RO_3(R_2O_6)$	Group 7. RH R_2O_7	Group 8. $RO_4(R_2O_8)$
		H							
	He	Li	Be	B	C	N	O	F	
	Ne	Na	Mg	Al	Si	P	S	Cl	
	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe Ni Co
		Cu	Zn	Ga	Ge	As	Se	Br	
	Kr	Rb	Sr	Y	Zr	Cb	Mo	—	Ru Rh Pd
		Ag	Cd	In	Sn	Sb	Te	I	
	Xe	Cs	Ba	La	Ce	(Nd,Pr)	—	—	— — —
		—	—	—	—	—	—	—	
		—	—	Ya	—	Ta	W	—	Os Ir Pt
		Au	Hg	Tl	Pb	Bi	—	—	
		—	Ra	—	Th	—	U	—	

which have resulted "by gradual condensations from a primary material." Until such a transformation of one element into another has been proven by experiment, chemists will still hold to the idea of indivisible elementary particles.

In the periodic arrangement of the elements, their physical and chemical properties are developed by the position of the element in the system. The most electro-positive

elements are placed to the left in each group, that character then vanishes as an acid-forming character appears until finally the strongly electro-negative elements (the non-metals) are found on the right in the group. Valency also finds full expression in this system. The table given on page 88 is the arrangement of the elements according to the Periodic Law.

Having brought the work of determining atomic weights of the elements up to the present, this subject of chemical research will be closed and a return made to 1800 in order to follow the second line of chemical endeavor which had its inception at that time:

THEORIES FORMULATED TO EXPLAIN CHEMICAL COMPOSITION.

Lavoisier
Radicals
$(CH_3)_2O$

Berzelius
Earlier Radicals
Dualistic Theory

Davy-Liebig-Graham
Definition of Acids

Dumas
Ætherin Theory

Berzelius-Liebig-Wöhler
Older Radical Theory

Dumas-Laurent
Substitution Theory

Laurent
Nucleus Theory

Dumas
Older Type Theory

Berzelius
Theory of Copulas

Gerhardt
Theory of Residues

Gerhardt-Laurent
Type Theory

Kekulé
Extension of the Type Theory

Kolbe
New Radical Theory

Kolbe-Frankland-Couper-Kekulé
Theory of the Saturation Capacity of the Elements or The Theory of Valency

Immediately following the announcement of the chemical atomic theory (1802—), it became evident to

chemists that a more thorough knowledge of the nature of compounds was imperative. As a result of the investigations of eminent chemists, who entered this field of chemical inquiry, theories were formulated which sought to explain the composition of these compound bodies. These theories were accepted and, as time passed on, were either merged into more plausible hypotheses or were dropped as they became inadequate.

At times, Dalton's atomic theory and its underlying principle—the atom—was forgotten. The observations of Gay-Lussac and others were laid aside. The hypothesis of Avogadro was neglected.

During this period a struggle for supremacy of doctrine was carried on by Berzelius and his school on one side against the French School on the other. It was a time of personal controversies; and yet withal there resulted a clearing of the sky at its close.

The first statement concerning the composition of compound substances was uttered, before 1802, by Lavoisier. He stated, "that the constitution of organic substances depended upon the existence of complexes or *radicals* in union with oxygen." Lavoisier was, therefore, the originator of the term "radicals." He emphasized the fact that oxygen was the important element in both inorganic and organic compounds. Berzelius accepted this idea that compounds were composed of radicals and oxygen, but added "that sulphur, or the halogens or negative groups of elements can be substituted for the oxygen which is without the radical." Berzelius was influenced by experiments which he had been conducting with the electric current upon inorganic compounds.

In 1818, Berzelius published his electro-chemical theory; and it is not strange that he combined the main

point of that theory with his ideas concerning "radicals." In 1820, he announced his "dualistic theory" which sought to explain the composition of compound substances.

The formula $(CH_3)_2O$ contains the germ of the guiding thought of all the theories entertained by Berzelius. In these theories the dominant idea is that compounds consist of two distinct parts which are electrically different. Berzelius applied this thought in explaining the constitution of inorganic compounds, for example, oxides were composed of the radical (metal or metalloid) and oxygen; salts were composed of a basic oxide (electro+) and an acid radical (electro−) $BaO.SO_3$, $ZnO.CO_2$. He further sought to explain the composition of organic compounds by the same hypothesis, which were said to consist of radicals in union with oxygen, sulphur, bromine, chlorine or groups of negative elements.

It is remarkable that the idea of radicals, first suggested by Lavoisier, is found in all of the theories formulated during the next sixty years. It is very evident in the nucleus and substitution theories, and it is even present in the type theory.

It is difficult to trace the development of any one of these theories alone. They are so intertwined that it is absolutely necessary to speak of them together. They are related, and these relations must be emphasized, and this cannot be done without frequent repetition.

In 1820, when the dualistic theory was completed, it had been extended to include the organic substances. Berzelius did not favor the idea that organic bodies were primarily due to the action of a living or vital force. He believed that the combination of elements into groups or radicals was the primary cause of their existence.

The first manifestations against the dualistic theory came from a consideration of "acids" begun by Davy, Gay-Lussac and Thénard. Lavoisier had stated that oxygen was the "acid principle."

Davy's discovery of the alkali metals and his experiments upon chlorine were the initial events in establishing the correct nature of acids and their salts. He thought that the alkali metals were elements, but after Gay-Lussac and Thénard proved the presence of hydrogen in ammonia, Davy was in doubt concerning these metals, and thought that they, too, might contain hydrogen. Gay-Lussac and Thénard proved the alkali metals to be elements.

Berthollet and Lavoisier believed that hydrochloric acid contained oxygen. When Davy, Gay-Lussac and Thénard began their investigations, hydrochloric acid gas was thought to contain chemically combined water. These three investigators failed to find oxygen either in the acid or in chlorine. Chlorine was thereafter added to the list of elements as well as iodine and fluorine. Hydrochloric acid they demonstrated to consist of hydrogen and chlorine only. Berzelius was not convinced. He believed in the *oxygen theory of acids* and he would not accept these statements as he saw in them a blow to his dualistic theory.

Davy and Dulong were making the attempt to bring the acids without oxygen and those containing oxygen upon some common ground.

Davy observed that iodic anhydride did not possess acid properties, but acquired them after union with water; he, therefore, concluded that *hydrogen and not oxygen was the "acidifying principle."* This was the beginning of the hydrogen theory of acids.

These opinions of Davy, concurred in by Dumas, were neglected for a time. In 1825, Berzelius had accepted, to some extent, the views of Davy and others, for he now included fluorine, chlorine and iodine among those elements which form salts. He drew a distinction, however, between *haloid salts* (salts which contained no oxygen) and *amphid salts* (salts which contained oxygen).

In the third decade of the nineteenth century, the opinions of Davy and Dumas concerning acids reappeared with new proofs. In order to explain the composition of acids upon a common basis, a definition was given which stated "that hydrogen was always a constituent of acids, and with it there was a radical." "The radical did not always contain oxygen." This so-called "hydrogen theory of acids" or the "hydrogen acid theory," of Davy was more clearly explained by Liebig, who used for the explanation a series of organic acids and studied the saturating capacity of each, and from these studies, he suggested that there was a possibility that a molecule of acid might combine with more than one molecule of base, and that among the organic acids there were some which perhaps contained more than one hydrogen atom with the power of exchangeability. He designated acids as monobasic, dibasic, tribasic, tetrabasic or pentabasic, according to the number of exchangeable hydrogen atoms contained in one molecule of the acid. Liebig, in this connection, profited by the work of Graham on phosphoric acid.

Liebig maintained that "acids are particular compounds of hydrogen, in which the hydrogen can be replaced by metals." Salts "are the products of such replacement of the hydrogen of acids. Neutral salts were those compounds in which the hydrogen is replaced by its equiva-

lent in metal. Acid salts were those in which there is a residuum of hydrogen atoms."

Salts should not be looked upon as consisting of basic oxides and acid oxides ($Na_2O.SO_3$). They were, rather, the products which resulted from the replacement of the hydrogen of acids previously in union with an acid radical. In this way Liebig demonstrated the similarity between the so-called oxygen acids and the haloid acids, and between the amphid and haloid salts. He disagreed with the dualistic notions of Berzelius.

Berzelius maintained that the haloid salts were in a class by themselves; that the amphid salts consisted of two parts—an acid oxide and a basic oxide. Barium chloride ($BaCl_2$) was a haloid salt, barium sulphate ($BaO.SO_3$) an amphid salt. Liebig, however, had placed all salts in one line. Berzelius objected to Liebig's unitary idea concerning salts. This caused an estrangement between Berzelius and Liebig. Berzelius always contended that Liebig's theory of acids and salts "led to the confusion of ideas, and stood in the way of a more perfect knowledge."

During the years following 1810 and especially those immediately following 1820, organic chemistry was growing in importance. Berzelius held that organic compounds like the inorganic were binary. In the former, compound radicals were joined together and these played the same rôle in the organic as the elements in the inorganic compounds. He thus extended his dualistic theory to include organic compounds.

Between 1820 and 1830 the first efforts were made to explain the composition of organic compounds by means of compound radicals, and these subsequently led to the establishment of the radical theory.

Gay-Lussac had investigated "cyanogen" and showed that as a compound radical it played the part of an element. He also expressed the opinion that alcohol consisted of ethylene and water. It had been observed that alcohol could be transformed into ether and ethylene. It was assumed, therefore, that ethylene was a constituent of both alcohol and ether. This idea of Gay-Lussac was further advanced by Dumas and Boullay.

In 1821, Dumas announced that ether consisted of C_2H_4 and H_2O. Berzelius was willing to accept this because he could compare it readily with $NH_3.H_2O$. Berzelius named the radical (C_2H_4)—"Ætherin." As a consequence, Dumas formulated his "ætherin theory," the basis of which was "that densities of alcohol and ether equaled the sums of the densities of ethylene gas and water:"

$$\text{Ether } \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} = \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} = H_2O.$$ Two volumes of ethylene plus one of water.

$$\text{Alcohol } \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} = H_2O.$$ One volume of ethylene plus one of water.

$$\text{Ethylene chloride } \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} = HCl.$$

The radical "ætherin" was thought to be present in all ethyl compounds; and it was compared to the inorganic radical "ammonia—(NH_3)."

Ammonium hydroxide $NH_3 = H_2O$ analogous to alcohol.
Ammonium chloride $NH_3 = HCl$ analogous to ethyl chloride.

Although this view of the constitution of organic compounds harmonized in a certain sense with the idea of Berzelius as set forth in the dualistic theory, he was unwilling to subscribe to the ætherin doctrine as finally stated by Dumas. This theory was not generally accepted. It lasted but a short time, chiefly because it could not be applied to the many new organic compounds which were being discovered. Another reason for its short life was that, according to it, C_2H_4 should be a very strong base and with water give a strong alkaline reaction; whereas alcohol (the body resulting from the union of C_2H_4 with water) was neutral.

The "ætherin theory," however, was the forerunner of the radical theory, in that it attempted a comparison upon common ground between organic and inorganic compounds. The development of the idea that organic compounds are composed of radicals was brought about principally by the researches of Liebig and Wöhler.

They announced the discovery of the radical of benzoic acid, it had the composition $(C_6H_5CO)^2$ and to it they gave the name "benzoyl." In the many transformations made with the "oil of bitter almonds," they found that this radical remained unaltered. This discovery not only aided in the development of the radical theory, but it exerted a wonderful influence upon the development of organic chemistry.

Berzelius was delighted with the discovery. He suggested that the radical be named "proin or orthrin" because it heralded "the dawn of a new day for organic chemistry."

When "benzoyl" was discovered, there was great rejoicing among the friends of Berzelius, and there was still greater joy when Wöhler and Liebig found that the

radical would combine with hydrogen, with chlorine, with hydroxyl, with the alcohol residues and that it was also possible for the radical to enter into union with itself.

In Hoffman's "Faraday Lecture on Liebig," when he discusses this discovery of the compound radical "benzoyl" his enthusiasm for these two chemists and for the results of their investigation is unbounded.

One can readily understand how the idea of compound radicals, as the fundamentals of organic chemistry, must have taken hold upon the minds of men. Liebig and Wöhler compared the radical "benzoyl" with potassium and other metals in the inorganic compounds. They accordingly wrote the oil of bitter almonds $C_6H_5CO.H$. The following is a list of compounds showing the transformations of this radical "benzoyl:"

$C_6H_5CO.H$ ..... Oil of Bitter Almonds
$C_6H_5CO.OH$ ..... Benzoic acid
$C_6H_5CO.Cl$ ..... Benzoyl chloride
$C_6H_5CO.NH_3$ ..... Benzamide
$C_6H_5CO.OC_2H_5$ ..... Benzoic ether
$C_6H_5CO.CN$ ..... Benzoyl cyanide

The immediate outcome of this discovery of the two German chemists was to introduce into theoretical chemistry the idea of compound radicals, which in organic chemistry act precisely as the metals do in the salts of inorganic chemistry, and, to urge chemists to search for other similar groups or radicals.

From such endeavors arose the "radical theory." The compounds related to alcohol furnished the best group with which to work. At this time, about 1833, Dumas believed that "ætherin" was the radical of alcohol and ether. Berzelius thought that alcohol and ether had

different constitutions. Liebig believed that the "ethyl" radical (written by him—C_4H_{10}) was common to both of these compounds. They all agreed, however, that compound radicals existed as distinct constituents of these compounds. The following facts, they held, must be true before a group of elements could be considered a "radical:"

(1) It must be either an element or a group of combined elements, which group remains after one or more elements have been removed from the compound.

(2) It must be possible to replace the radical by a simple substance.

(3) If the radical is in combination with a simple substance, it must be possible to replace that substance by some other simple substance.

In addition to these facts, Berzelius claimed that a radical was unalterable, but Liebig did not wholly concur in this belief.

The year 1837 found the radical theory at its height. Dumas was convinced of the uselessness of his ætherin theory. He joined Liebig with a view of investigating organic substances. They both regarded "*organic chemistry as the chemistry of compound radicals.*"

In 1839, Bunsen's investigations of cacodyl compounds considerably aided the radical theory.

The preceding paragraphs give the state of affairs existing when Dumas began investigating radicals. Gay-Lussac, Faraday, Liebig and Wöhler had noted the action of chlorine upon certain organic compounds and

had observed that hydrogen escaped in amount equivalent to the chlorine which entered the compound.

In 1834, Dumas, after investigating the action of chlorine upon turpentine and the production of chloral from alcohol, declared:

"When a compound containing hydrogen is exposed to the action of chlorine, bromine, or iodine, it takes up an equal volume of chlorine, or bromine, etc., for each atom of hydrogen that it loses.

"If the compound contains water, it loses the hydrogen of this without replacement."

Dumas, in 1835, extended this statement to one which is the basis of his "substitution theory"—"that in chemical reactions, generally, an exchange of equivalents of one element for equivalents of others takes place."

Laurent proceeded further, he stated, "that the structure and chemical character of organic compounds are not materially altered by the entrance of chlorine and the separation of hydrogen." This observation together with the view that chlorine takes the place of the substituted hydrogen constitute the core of the substitution theory. The theory belongs more to Laurent than to Dumas, for the latter, when attacked on this point by Berzelius, denied having any share in that portion of the theory which stated that the chlorine in taking the place of the substituted hydrogen caused no material change in the character of the compounds thus acted upon.

The discovery of trichloracetic acid ($C Cl_3 . COOH$) by Dumas gave considerable aid to the establishment of this new doctrine.

Thus the fact that chlorine could be introduced into

acetic acid for hydrogen, and an acid still remain which would form salts with metals, led Dumas to agree with Laurent, his pupil, that the only change which the acid had sustained was that the positive hydrogen atoms had been replaced by negative chlorine atoms. Berzelius was unable to reconcile this thought with the dualistic notions based as they were upon his electro-chemical theory. The idea of replacing electro-positive elements with electro-negative elements was untenable. He, also, considered that a compound in which oxygen was a fourth element was at once an oxide and a sesquichloride; therefore, trichloracetic acid was, in his opinion, a copulated compound of sesquichloride of carbon with sesquioxide of carbon.

Dumas said, however, "that acetic acid was at low temperatures a leafy, crystalline mass, melting at 16.7 and yielding at the same time a penetrating acid-like liquid." The trichloracetic acid made from this acetic acid by the action of chlorine upon it in the sunlight, was also a body that crystallized and showed properties similar to those manifested by the parent, acetic acid. The only way to account for the existence of this body was on the assumption that the negative chlorine had taken the place of the positive hydrogen.

Berzelius asserted that trichloracetic acid had not been produced by substituting negative chlorine for positive hydrogen in the parent acid, but that it had been formed by chlorine atoms attaching themselves without the radical.

Gerhardt and Laurent, at this time, contributed much of the experimental work which in the end brought about the acceptance of the ideas embodied in substitution and caused the overthrow of dualism. Berzelius was exhaust-

ing himself with fruitless discussions, while in France these two men (Gerhardt and Laurent) were making discoveries and accumulating evidence against the dualistic notions which Berzelius was so zealously guarding.

Malaguti and Regnault had prepared dichlorformic ether and other complex bodies, which could not be explained by the idea of dualism, but which could be made clear on the basis of substitution.

In 1842, Melsens, by converting trichloracetic acid into acetic acid, gave decisive evidence as to the truth of the principle of the substitution theory. During the years (1832–1842), there was a division of opinion among chemists as to the relative merits of the existing theories. Some inclined to the French School; others to the ideas of Berzelius, Liebig or Gerhardt; and others, taking no active part, waited for the heavens to clear. It was then that Wöhler, for the first time, permitted himself to express an opinion in regard to a debated question. A letter signed S. C. Windler appeared in Liebig's "Annalen:" Wöhler wrote it as a private communication to his friend Liebig. It was dated from Paris. In it the writer announced: "I have succeeded in replacing in manganese acetate not only the hydrogen by chlorine, but also the metal, and finally the carbon and oxygen too; the product, although consisting of chlorine only, exhibited all the characteristic properties of the original salt . . . by passing chlorine in the sunlight into a solution of copper acetate, I obtained, as was to be expected, the copper salt of Dumas' chloracetic acid. On heating this in a current of dry chlorine, oxygen was liberated, a yellowish mass being formed consisting of chloro-copper chloracetate. On continuing the action of chlorine the metal was also replaced and chlorine chloracetate was formed,

crystallizing in small, brilliant, golden-yellow prisms. This was, however, not the final product, inasmuch as by treating it in an aqueous solution with chlorine for two weeks longer, carbolic acid was evolved, and in cooling the liquid to 2° it deposited crystals, having all the properties of chlorine hydrate."

To which may be added a few lines of a letter from Wöhler to Berzelius in 1840:

"The chemical bother and talk, the eternal song of the substitutions makes me quite sick, and how many of the statements are only guess-work, only assertions, and yet put down as facts."

Throughout all of the discussions upon substitution, Berzelius insisted that electro-negative elements could not displace electro-positive ones. According to the recent assertions of Julius Thomsen, there exists in the chlorine molecule, electro-negative chlorine in union with electro-positive chlorine. The same is true of the hydrogen molecule. When, therefore, chlorine enters a compound, such as benzene, and substitutes hydrogen, it displaces electro-positive hydrogen and electro-positive chlorine enters to combine with the electro-negative hydrogen that remains. If this is true, Berzelius was correct.

Liebig abandoned the dualistic ideas of Berzelius slowly. He and Wöhler had contributed much in laying the foundation of the radical theory; and an organic chemistry which was a chemistry of compound radicals was wholly acceptable to them. The chemists of the French School were, however, discovering many new substances which could only be regarded as substitution products.

As time progressed, Liebig, Wöhler and others reluctantly renounced dualism and subscribed to the main points of the substitution theory.

Immediately following the general acceptance of Dumas' substitution theory, Laurent advanced a new theory—the "nucleus theory"—first published in 1836.

Laurent claimed that "All chemical bodies have a definite ground form. They consist of a central nucleus, in which the individual elements can be replaced by other elements, and grouped around this central nucleus are other nuclei."

According to Laurent, compounds had form. He was the first to suggest "space chemistry." His explanations are not clear, but they are the first indications of "geometrical isomerism."

According to Wöhler, Laurent's nucleus theory was based entirely upon substitution.

This theory never met with very general approval. It was based upon the radical theory and included the idea of substitution, but it vaguely suggested a new thought—that of space chemistry.

Laurent proved that radicals could be altered. His efforts to classify organic compounds on uniform principles were helpful. His views would have fallen into oblivion if it had not been for Odling and Gmelin. Gmelin, in Germany, thought the teachings of the French School merited consideration; he was so deeply impressed with Laurent's nucleus theory that he included it in his text-book. Odling was determined that the ideas of Laurent should reach the chemical students of England; he translated Laurent's "Chemical Method," which was published by the Cavendish Society, as was also a translation, by Henry Watts, of Gmelin's text-book, "Hand-Book of Chemistry."

Extracts From the Hand-Book of Chemistry by Leopold Gmelin.

"The atoms of organic compounds are either nuclei or compounds of nuclei with various substances attached to them externally.—Laurent. [It is only fair to say that Laurent frequently designated nuclei by the term *radicals*. This application has a tendency to confound them with the radicals of the radical theory, from which they differ in reality very materially. The *nuclei contain an even number of atoms*, the *radicals an uneven number of atoms*.—Gmelin.]

"The number of carbon atoms in the nucleus bears a relation to that of the other atoms. If the nuclei contain hydrogen, in addition to the carbon, they are *primary nuclei*. But if one or more of the hydrogen atoms of the nucleus are replaced by atoms of other elements or of certain compounds, organic or inorganic, which take the same place in the nucleus that the hydrogen atoms originally occupied, the compound atoms thus formed are called derivatives or *secondary nuclei*. Hence, in the theory of nuclei, less importance is attached to the nature of the elements than in the radical theory; more importance being attached to their *configuration*. The elements, which usually replace the hydrogen atoms in the nucleus are chlorine, bromine, iodine, oxygen, nitrogen and the metals. When the hydrogen of a nucleus is replaced by a compound, each atom of hydrogen is replaced by one atom of the compound. The compounds capable of replacing hydrogen in the nucleus are NO^4, NH^3, C^2N, etc. . . . When, by the action of various substances, one nucleus is converted into another without loss of carbon, the new compound cannot be represented

by a formula, in which the nucleus is supposed to contain a number of carbon atoms different from the former. When, on the contrary, a portion of the carbon separates from the nucleus in the form of carbonic acid, the old nucleus must be replaced by another containing a smaller number of carbon atoms and, therefore, standing lower in the organic scale. When decomposition takes place in such a manner that the hydrogen, withdrawn from the nucleus, is replaced by an equal number of atoms of chlorine, etc., the nucleus remains the same, but is transformed more or less into a secondary nucleus. When, however, hydrogen, or chlorine, etc., is withdrawn without substitution, the residue, if still an organic compound, must belong to the series of another nucleus. The replacement of a certain number of atoms of hydrogen in the nucleus by chlorine, bromine or iodine does not alter the elements of the compound as much as the replacement of an equal number of atoms of hydrogen, by oxygen, etc. Moreover, all nuclei are neutral, even when they contain oxygen, chlorine, bromine, NO^4, etc." —Laurent.

It was in the 30's when Laurent's theory of nuclei was introduced, and he declared that it was possible to introduce NO_2 for one atom of hydrogen in a compound because the *space* occupied by the hydrogen atom with its heat sphere is sufficient space for the other substance with its heat sphere, provided the heat sphere of the atoms of the new substance entering take up less space than the hydrogen or an equal space. Further, chlorine, bromine, iodine or sulphur might combine with the nucleus to the number of from two to six atoms. These

elements may be removed by potash without the substitution of another substance.

"These additions of chlorine to the nucleus may be removed by the potash without substitution of another substance. If ethylchloride is treated with caustic potash the hydrochloric acid is drawn out to form potassium chloride and water, and the original nucleus C^4H^4 is restored."—Laurent.

It is now known that C_2H_4 treated with hydrogen bromide or chloride yields monochlorethane or monobromethane. Laurent and the chemists of his day did not know these unsaturated bodies of the first, second and third degrees.

"Laurent's Classification of Organic Compounds.

"Organic compounds may be arranged in series. The basis of each of these series is a primary nucleus, together with its secondary nucleus. The compounds of the same series contain the same number of atoms of carbon." For example, the *ethylene series*,—ethylene—C^4H^4 [C_2H_4]. When water is added externally to ethylene, alcohol results—C^4H^4, H^2O^2 [C_2H_5OH].

"Each series contains compounds belonging to different types. The nucleus type includes all nuclei, primary or secondary; the alcohol type, all nuclei to which water

(H^2O^2) has been added; the monobasic acid type, all nuclei which have taken up 4 O in addition and so on.

"A primary nucleus may be altered by abstraction of 2H; the remainder is the *Characteristic* (Car.), which, in the case of methylene, C^2 H^2, is merely C^2, while in other nuclei it is C^2+ the remainder of the hydrogen. The 2H are the *Constant;* so that every primary nucleus = Car. + Const. = Car., H^2. Hence, the compounds of any series may be arranged and designated as follows:— Nuclei. . . Halydes. . . Hydrides. . . Anhydrides. . . Holoformes, Amides, etc."—Laurent.

"I have considered it my duty to explain the more important doctrine of Laurent's theory," says Gmelin, "more especially as the theory has not in Germany, at least, the attention it merits. Whoever will submit it to the test of examination will admit that the nucleus theory of Laurent is the one that gives the most simple, the most comprehensive view of the many thousands of organic compounds and unites them with the most natural families or series. With my own idea this theory is in peculiarly close accord."

Laurent had endeavored to represent substances by means of figures: "Imagine a right sixteen-sided prism, and in each angle one atom of carbon, making in all thirty-two atoms of carbon; in the middle, between each two angles, one atom of hydrogen, making altogether thirty-two atoms of hydrogen; and lastly, on each base

of the prism, one atom of OH, forming pyramids. Thus the compound equals $C^{32}H^{32}.2$ OH. In the same manner as crystals may be cleft mechanically, and the primary nucleus separated from the secondary envelope, . . . so likewise, may a chemical separation be made. After the removal of the two pyramids OH, there remains the primitive form (the germ or nucleus). Chlorine or oxygen acting on this primitive form withdraws the hydrogen; the prism would then fall to pieces, if the hydrogen atoms were not replaced by atoms of chlorine or oxygen. The HCl or OH may either pass off or form pyramids, on the prism, which, however, may be removed by chemical division."—Laurent. "Further than this, Laurent . . . made no attempt to assign definite figures to particular compounds. Gerhardt . . . considerably extended them. He suggested that an effort be made to apply the nucleus doctrine to inorganic compounds. If it should answer in the inorganic field, it will be strengthened."—Gmelin.

Gmelin, using Laurent's nucleus theory as a basis, discusses the relative position of the elementary atoms in inorganic compounds. He greatly extended Laurent's ideas concerning the arrangement of atoms in space. Gmelin is uttering the first important statements in *spacial chemistry* thirty years prior to the first announcements made by van't Hoff and Le Bel (1874).

Concerning inorganic compounds, Gmelin writes, "The crude chemical formula of sulphate of potash is KSO^4 (K_2SO_4), the rational formula of Berzelius is KO, SO^3 ($K_2O.SO_3$), if the compound be regarded as sulphate of

potash; K, SO^4 (K_2. SO_4) if it be regarded as sulphanide of potassium; and KS, O^4 (K_2S. O_4) if it be regarded as oxidized sulphide of potassium. Now whichever of these three rational formulæ be adopted the mode of writing the formula gives no satisfactory idea of the manner in which the atoms are actually combined. The three substances in the formula might be arranged in a straight line, KO, SOO ($K_2O.SOOO$), but in nature they are doubtless united in a body of three dimensions; for their mutual affinity induces the greatest possible approximation of the heterogeneous atoms. Nearly all chemists adopt the atomic theory; they determine the relative weights of the atoms, and their relative distances one from the other, or the relative spaces occupied by each atom of the compound substance, including the surrounding calorific envelope; hypotheses are also made respecting the form of the atoms, etc. . . . Why then should we not throw out suggestions in regard to relative positions of these atoms."

Gmelin continues, "It may be assumed that the heterogeneous atoms of a compound will approach as near to each other as their affinity requires, and the elasticity of the calorific envelope allows, and that they will take up that particular position with regard to each other, which allows of the greatest and most varied approximation of the heterogeneous atoms. Two atoms, such as hydrogen and oxygen, H and O, can only be disposed in a line, horizontally or vertically. The same is true in regard to two atoms of one substance and one atom of another substance MnO^2, here the manganese lies in the middle, one atom of O to the right and one atom of O to the left, O-Mn-O. One atom of one substance and three of another, such as SO^3 would probably form a plain triangle

with the sulphur atom in the middle. With one atom and four atoms, as in NO^4, a tetrahedron can probably be formed. Nitrogen in middle and oxygen at the four corners. With one atom and five atoms as PO^5 (P_2O_5), we would have phosphorus in the middle, one atom of oxygen above and one atom below and three atoms of oxygen disposed horizontally round the phosphorus atom.

"When this and similar compounds of the first order unite together, for example to form salts, we may imagine that in many cases the relative position of the atoms no longer remains the same, but is so far altered that the tendency of the heterogeneous atoms to approximate as closely as possible is satisfied to the utmost. Thus, in the combinations of KO (K_2O) and SO^3, a compound atom is probably formed, in which the sulphur is placed upon the potassium and the three oxygen atoms are horizontally around the points of contact. Similarly with KO, SO^3 ($K_2O.\ SO_3$), excepting that in this instance the four oxygen atoms are placed in a square around the point of union of KS, so that a double four-sided pyramid is formed. . . . Use balls of wax," says Gmelin, "variously colored to represent different atoms and then arrange them as just suggested." Is not this *space chemistry?* To-day, models are used in order to explain the peculiar isomerides, and the bodies which occupy the solid angles are differently colored from those which occupy central positions.

"The tendency of heterogeneous atoms to approximate as closely as possible, causes them to assume the most simple arrangement that their number will admit. That the crystals of sulphate of potash assume in spite of this arrangement of the double four-sided pyramid, a form belonging to the right prismatic, instead of the square

prismatic system, arises perhaps from the sulphur having a much larger atomic number than the potassium, and consequently a much smaller specific or atomic volume, in consequence of which the vertices of the two pyramids are dissimilar.

"This supposition respecting the aggregation of atoms in sulphate of potash, may perhaps terminate the controversy as to whether that compound is KO,SO^3 ($K_2O.SO_3$) or KS, O^4 ($K_2S. O_4$). According to the above hypothesis it is neither of the three, but rather KO^4S (K_2O_4S). The atoms, indeed, are united in such manner that we cannot assert which oxygen atoms belong to the sulphur and which to the potassium. At first view, it might appear that the third formula KS, O^4 ($K_2S. O_4$) is admissible, but in sulphide of potassium, the potassium and sulphur are probably more closely united than in the sulphate of potash, in which the four surrounding oxygen-atoms interpose themselves to a certain extent between the potassium and the sulphur. For the rest, until the above hypothesis shall have been put to the test of experience, which may be best done by comparing the crystalline forms of salts with the assumed form and arrangement of their atoms—preference must be given to the first of the three preceding formulæ, namely KO, SO^3 ($K_2O. SO_3$), inasmuch as it has always been adopted hitherto, and in the rest, the objections outweigh the advantages. Oil of vitriol would be similarly constituted, the potassium being merely replaced by hydrogen.

"This theory may perhaps lead to an explanation of the three isomeric states of phosphoric acid.

"If we now apply to organic compounds the principles above illustrated, by examples taken from inorganic chemistry, and assume with Laurent, that these compounds

may be divided into organic nuclei and compounds of these nuclei with substances externally attached to them, we shall find that, in the nuclei, the carbon-atoms must be united with the other elements composing the nucleus, in such manner as to allow the heterogeneous atoms to approach the nuclei in as many ways as possible, whereby a determinate figure must be produced.

"The nucleus, ethylene C^4H^4 (C_2H_4) may serve as an example. It probably has the form of a cube, four angles of which consist of carbon atoms, and the four others diametrically opposed to them of hydrogen atoms. . . . To the ethylene series belong among other compounds aldehyde, alcohol and acetic acid, the crude formulæ of which are $C^4H^4O^2$, $C^4H^6O^2$ and $C^4H^4O^4$ (CH_3CHO, C_2H_5OH, CH_3COOH). These three compounds may, with some degree of probability, be supposed to contain the secondary nucleus C^4H^3O, one angle of the cube consisting of oxygen. This cube-summit formed of an atom of oxygen may be called an O-pole; and the summit diagonally opposed to it and formed of carbon, a C-pole. According to this supposition, the rational formula of alcohol would be C^4H^3O, H^3O, . . . The 3 H, in consequence of their peculiarly strong affinity for the O, are disposed on those three faces of the cube, one angle of which is formed by the O-pole while the external O-atom places itself upon the carbon-pole.

"The rational formula of aldehyde, determined in similar manner, is C^4H^3O, HO; the H-atom is attached to the O-atom of the nucleus, and the O-atom to the C-pole. . . .

"Acetic acid, would in the same manner be regarded as C^4H^3O, HO^3 or more precisely, as O^3, C^4H^3O, H, the 3 O being disposed on those three faces of the cube

which consists only of C and H atoms, and 1 H on the O-atom of the nucleus.

"Alcohol, by the action of 2 O, is converted into aldehyde and 2 HO; and this aldehyde, by the further addition of 2 O, is converted into acetic acid. The first 2 At. O, together with 2 H out of the three external H-atoms, form 2 HO; the third of these external H-atoms is transferred from the cube-face to the O-atom of the nucleus, and aldehyde is thus formed. If 2 more O are added, they dispose themselves on two of the cube-faces consisting only of C and H, while the O-atom attached to the C-pole is transferred to the third cube-face, and thus acetic acid is formed."

Gmelin thought that when acetic acid was neutralized with potash, the resulting compound would be "O^3, C^4H^3O, K;" the external atom of hydrogen having been replaced by potassium, with the formation of water. In this he differs from Laurent, who believed that all of the hydrogen atoms of acetic acid were within the nucleus, "$C^4H^4O^4$ and that potassium, therefore, entered the nucleus—C^4H^3K, O^4."

In explaining the substitution of the hydrogen of acetic acid by chlorine, Gmelin says, "in this case, it is obvious that the H-atom which is replaceable by a metal remains unaltered.

"This difference of comportment between the one H-atom and the other three is explained by their different arrangement." The hydrogen atom which may be replaced by metal is different because it touches only the oxygen atom of the nucleus.

"Moreover, in consequence of the very close proximity

which exists between the simple atoms of an organic compound, it is probable that the result is determined not only by the affinity of the atoms lying immediately together, but also, though in a less degree, by that of the more distant atoms. . . . Finally, to consider one of the most complicated cases, the formation of a compound ether: Alcohol and Acetic acid form 2 At. water and 1 At. acetic ether. . . . Here we must suppose that the carbon-pole of the alcohol first approaches the oxygen-pole of the acetic acid, so that the former may give up the external O-atom there situated to the external H-atom on the O-pole of the acetic acid; in the next place, the alcohol and acetic acid—a cube-face of the one being turned towards a cube-face of the other—must turn round in such a manner that the C-pole of the alcohol and the O-pole of the acetic acid may move away from one another, and the O-pole of the alcohol and the C-pole of the acetic acid approach one another. In this movement, one of the three external H-atoms surrounding the O-pole of the alcohol, comes in contact with one of the external O-atoms surrounding the C-pole of the acetic acid; these atoms unite in the form of a second atom of water, and are eliminated; and the cube-face of the alcohol thereby exposed attaches itself to the simultaneously exposed cube-face of the acetic acid; and in this manner 1 At. acetic ether is produced. Hence this compound, being formed by the juxtaposition of two cubes, has the form of a square prism. On two of the opposite lateral edges of this prism, there are situated in succession, supposing the acetic acid to be at the top, CHCH: on the third: OCHC: on the fourth: HCOC. On this last edge, however, there are likewise two external O-atoms belonging to the acetic acid, at the top, and two

external H-atoms, belonging to the alcohol, at the bottom, hence this last edge exhibits this arrangement:

O H
H CO C
O H

Of the compounds of the "methylene series," Gmelin writes, "In this case, we may suppose that methylene has the shape of a square table, the four corners of which are formed of a C-atom and an H-atom alternately. In marsh-gas, two more atoms of H are attached to the nucleus, making C^2H^2, H^2 (CH_4); of these 2 H, one is attached to the upper, the other to the lower surface of the square table; and if the figure be so placed that one of the C-atoms shall be alone and the other below, the 4 H will be arranged horizontally around the point of contact of the 2 C so that an octahedron will be formed.

"These examples taken from the ethylene- and the methylene-series may suffice, for the present, to give a general idea of the view which I entertain of the constitution of organic compounds. . . . Even if the data of this investigation are defective or erroneous, I am yet convinced, that all theories on the constitution of organic compounds, and all controversies as to this or that mode of writing rational formulæ, if not supported by a plausible arrangement of the compound atom, will aid us but little in the acquisition of correct ideas."

The writings of Gmelin are full of interest. The nucleus theory is forgotten to-day, but one thought contained in Laurent's writings, "that atoms might arrange themselves according to a form," has been re-

vived in recent times. This idea introduced by Laurent was made clearer and greatly extended by Gmelin. He explained the constitution of inorganic as well as organic compounds by means of "geometrical figures." The moment that the figure of sulphur trioxide is drawn in accordance with the recommendation of Gmelin, the moment a triangle is constructed and on its solid angles are placed balls of colored wax, that moment there is being performed precisely what van't Hoff, Pasteur, Le Bel and Baeyer did at a much later time.

The life of the nucleus theory was short. "Substitution" was still a subject of discussion. Following close upon the nucleus theory, Dumas proposed a theory, which he called the "older type theory." Dumas was led to formulate this theory after his study of trichloracetic acid. He concluded that "there are in organic chemistry certain types which remain unchanged, even when their hydrogen is replaced by an equal volume of chlorine, bromine, or iodine." The term "chemical type" did not satisfy Dumas, and he introduced the term "mechanical type." The "mechanical type" included all compounds derived from one another by substitution, but differing in properties.

This theory survived a short time only. Berzelius was still opposed to those principles which were contrary to his cherished beliefs. Dumas declared Berzelius' "dualistic theory wrong." "Every chemical compound," said Dumas, "forms a complete whole and cannot, therefore, consist of two parts. Its chemical character is dependent primarily upon the arrangement and number of the atoms, and in a lesser degree upon their chemical nature."

Berzelius would not accept these utterances. Liebig,

who did admit the fact of substitution, would not consent, however, to the most extreme assertions of Dumas. For five years following 1838, Berzelius tried to combat these ideas of substitution and of types; standing, at times, upon ground both unsafe and untenable. He would not agree that trichloracetic and acetic acids had the same constitutions. After Melsens' work in 1842, Berzelius was compelled to admit that he was in error. He made a brave effort to save his cherished ideas in a "theory of copulas." Berzelius was, however, compelled to admit that chlorine could substitute hydrogen in the copula. This theory was much derided and Berzelius found that his adherents were unwilling to follow him. He then suggested that there was far too much speculation and not enough experimentation on the part of chemists.

Laurent had carefully studied all of the existing theories before he formulated his theory of nuclei, and he was as dissatisfied with that theory as were his contemporaries. It will perhaps be of interest at this point to learn how Laurent viewed some of the theories which have thus far been presented. In a most interesting volume, entitled "Chemical Method," these observations are found:

"According to some chemists, compound bodies are formed of two groups of atoms maintained in connection with one another by an electrical force, one of the groups being positive, and the other negative.

"According to other chemists, the atoms form but one single group, they are arranged therein in a symmetrical manner and have a certain relation to the crystalline form of the body. I will not stop to inquire whether the atom of sulphur is positive towards that of oxygen and negative towards that of potassium, whether two atoms when brought into union by their opposite electricities can

remain indefinitely attached to one another by means of the same force, whether atoms have, like the mineral tourmaline, two poles—the one positive and the other negative—or whether or not they are surrounded by an electric atmosphere. One primary question controls the whole inquiry. In order to determine the arrangement of the atoms which constitute a compound, it is evident that we must first be fully acquainted with the number of those atoms and consequently with their weight. . . . . There are greater probabilities in favor of the atoms of Gerhardt than in favor of those of Berzelius. Consequently, it is probable that nitric acid does not contain water, and that dualism is leading us into error concerning the arrangement of atoms.

"The chemists who uphold dualism are far from being agreed among themselves. All of them in maintaining their opinions rely upon the phenomena of chemical reaction, and for a long time the uncertainty of this method has been pointed out. It has been shown repeatedly that the atoms put into movement during a reaction take, at that time, a new arrangement, and that it is impossible to deduce the old arrangement from the new one. It is as if in the middle of a game of chess, after the disarrangement of all of the pieces, one of the players should wish, from the inspection of the new place occupied by each piece, to determine that which it originally occupied.

"It is reiterated everywhere at every moment that salts are obtained by combining acids with bases, that we can decompose them by separating the acid from the base, and that consequently, they contain two groups, the one negative and the other positive; the one acid and the other alkali.

"Now, let me remark that there is scarcely one salt in a thousand that has been obtained by the direct combination of its acid with its oxide, and still fewer that can be decomposed into an acid and an oxide, for even in making potassium sulphate, it is always hydrogen sulphate and hydrate of potassium that are employed. I deny the possibility of preparing this salt by means of the anhydrous acid and oxide. I affirm that this often quoted illustration has never been submitted to experiment and that the majority of salts cannot be made in this way with the anhydrous oxides and acids. And, besides, what is proved by this possibility of preparing certain salts by combining directly the acids and bases? If the manner in which the salts was formed and decomposed allowed us to determine the arrangement of its atoms we might maintain, first, that potassium sulphate is a combination of potassium sulphite with oxygen; second, that potassium sulphate is a combination of potassium sulphide with oxygen, since it can be prepared from these two bodies, and, moreover, when heated with charcoal it is transferred into sulphide; and third, that it contains K_2SO_4, etc.

"Of all these hypotheses, there is not a single one incapable of having reactions adduced in its support. Thus, if we choose to adopt the theory of Longchamp, according to which the oxygen salts contain the metals in the state of binoxide, we could prove by uniting sulphurous acid with binoxide of potassium that potassium sulphate contains $K_2O_2.SO_2$, and we could explain its decomposition with chloride of barium by the aid of the following equation:

$$K_2O_2 . SO_2 + BaCl_2 = BaO_2 . SO_2 + K_2Cl_2$$

If we had to explain the formation of potassium sulphate from potassium sulphide and oxygen, we could say that this last body acted upon the sulphur and burned it as if it had been uncombined and at the same time acted upon the potassium and converted it into a binoxide.

"We could prove by synthesis that hydrated nitric acid is a combination of peroxide of nitrogen with oxide of hydrogen. We could prove the same thing analytically by decomposing the acid by heat, when it would be resolved into peroxide of nitrogen, water and oxygen. In this case we should remark that the occurrence of water was due to the binoxide of hydrogen having undergone decomposition by reason of the heat employed.

"An objection might be raised to Longchamp's view inasmuch as many of the acids admitted to be present in the salts do not exist in the free state, but precisely the same objection could be advanced against his adversaries.

"The partisans of dualism do not, however, yield to these reasons, and contrive the following means to combat them:

"'To study the constitution of a binary compound we cannot,' say they, 'react upon it with any substance that first presents itself, but *we must* employ for the purpose a single body; and in order to study the constitution of a salt *we must* employ a base and an acid. Then, as bases replace bases and acids replace acids, it is clear that salts consist of bases and acids.'

"*We must* employ a base and an acid? And why must we do so? This they do not tell us, and for my part, I choose to employ simple bodies in my study of the constitution of salts. I choose to put iron in contact with sulphate of copper, and as the first metal replaces the

second, I embrace the system of Davy, and I conclude with him that sulphate of copper is constituted thus: $Cu . SO_4$.

"I *now choose* to take binoxide of barium and to react with it upon the same salt, and as by this means binoxide of copper is formed, I maintain with Longchamp that sulphate of copper contains sulphurous acid and binoxide of the metal: $CuO_2 . SO_2$.

"I *now choose* to carry out your method. I pour sulphuric acid into potassium hyposulphite, and as reaction gives rise to sulphur and sulphurous acid I conclude that the salt is formed of three groups, $S . K_2O . SO_2$, and that the trinitary system ought to replace the dualistic system.

"I previously remarked that there is scarcely one case in a thousand where anhydrous oxides and acids can be employed for the preparation of salts or obtained by their decomposition. To overthrow this objection, however, several experiments have recently been made, and the old inference arrived at. That is to say, chemists have succeeded in decomposing carbonate by anhydrous sulphurous and sulphuric acids, and as the carbolic acid is displaced from its combination without the recurrence of water, they have concluded that it existed ready formed in this carbonate.

"It is astonishing how at this day we should be compelled to attract attention to the most ordinary phenomena of chemistry, that we should be obliged to point out that one metalloid can displace another analogous metalloid, that one metal can drive out another metal, that an oxide can drive out an oxide, a peroxide expel and originate another peroxide, a hydrated acid give origin to another hydrated acid, that a salt produces another salt, etc.,—in

one word, that a body that fulfills a certain function always does by its action upon a salt tend to displace or give origin to another body fulfilling the same function, and if this displacement does not invariably take place, it is easy to say that the exceptional cases arise solely from the instability of the body intended to be thus displaced. For instance, at a certain temperature sulphuric acid by its action upon nitrate of potash gives rise to hydrated acid, but at a higher temperature this last acid cannot longer exist and consequently other products are formed.

"If, from such simple combinations as the sulphates and the carbonates, we pass on to the phosphates and the borates and the silicates, we shall still recognize the endeavor to construct binary groups, each of which is itself composed of other binary groups, but the number of atoms become greater and the number of hypotheses concerning their arrangement increases in the same proportion.

"We have a silicate which contains $Si_{13}O_{68}Mg_{21}Al_4H_{30}$, and we discuss seriously whether the atoms have this arrangement

$$((11\ SiO_2+21\ MgO)+2\ (SiO_2+Al_2O_3)+15\ Aq)$$

or this

$$(7\ (SiO_2+3\ MgO)+2\ (3\ SiO_2\ .\ Al_2O_3)+15\ Aq)$$

or this

$$(7\ (SiO_2+3\ MgO+2\ H_2O)+2\ (3\ SiO_2\ .\ Al_2O_3)+Aq)$$

or a hundred others. What is there to prove that the silica is distributed into three principal groups, that the magnesia forms two distinct combinations and that the water occupies two different places? (I believe that I am mistaken and that the water occupies one and twenty

places.) Does this salt by its reactions split up into a magnesian silicate on the one hand and an alumino-magnesian silicate on the other, etc.?

"I have often read the discussions which have taken place on this subject, and I avow that I have never found anything but what was either arbitrary or according to routine. . . . If from mineral we pass to organic chemistry, we shall see that in this division the arbitrary reigns supreme. Here also are reactions appealed to as a means of discovering the arrangement of atoms, but, like the ancient oracles, one single reaction serves two purposes, proving both the 'for' and the 'against.'

"As an illustration of the disorder that prevails in organic chemistry, I need merely state that acetic acid, one of the simplest of the acids, has been represented as the result of the arrangement of atoms as follows:

$C_4H_6O_3 . H_2O$	$(C_3H_6O)CO_2 . H_2O$
$C_4H_6O_4 . H_2$	$C_4H_2 . O_4$
$C_4H_6O . O_2H_2O$	$C_2H_4 . O_2$
$(C_2H_6)C_2O_3 . H_2O$	$C_4H_6O_2 . H_2O_2$
$(C_2H_6)C_2O_4 . H_2$	$C_4H_2 . O_4H_6$

For the support of every one of these formulas certain reactions have been invoked, and curiously enough, in several cases the reactions that are contrary to the hypotheses are precisely those which have been adduced for its formation. Thus, the formula $(C_3H_6)C_2O_3 . H_2O$ represents a combination of oxalic acid with an imaginary compound, C_2H_6; but nevertheless, we know very well that we cannot by any reaction demonstrate the presence of oxalic acid in acetic acid. It must be that for the maintenance of my cause, I have adduced the obscure hypothesis of an obscure chemist. No! The above is the hypothesis of Berzelius and of his school.

"Lastly, for the discovery of the arrangement of the atoms in a body, chemists do not even wait until it has been submitted to a certain number of reactions. Its centesimal proposition alone suffices for them.

"Some years back the discovery of an essence was announced, which essence contained $C_9H_{10}O_8$. Without waiting for further inquiries it was at once set down as a hydrated oxide—$3C_3H_2 . O . 2H_2O$. Subsequently, we were told that the substance was an acid, and its formula quickly became $C_{18}H_{18}O_5H_2O$. Some days after, the essence was announced to be an ether, and in the twinkling of an eye, the ether arrangement was given—$C_{14}H_{10}O_5 . O_4H_{10}O_2$, or better still, $C_2O_4(C_{12}H_{10}) . C_4H_8+H_2O$. From which, we learn that C_{12} and H_{10} are an intimate combination, while C_2 and O_4 are united in an ordinary manner; that C_2O_4 copulated with $C_{12}H_{10}$; that $C_2O_4(C_{12}H_{10})$ is conjoined with C_4H_8; and lastly, that the whole forms a 'marriage of convenience' with H_2O.

"Have we at last, I will not say a rule, but even a convention which can determine in this way the arrangement of atoms? No! Every chemist follows his own particular course and changes his formulas as often as he obtains a new reaction. We should arrive at results just as satisfactory by putting the atomic letters of a formula into an urn and then picking them out haphazard and forming dualistic groups.

"Next to reactions, chemists thought they had discovered in the galvanic battery a sure means of discovering the arrangement of atoms, but here we perceive an almost incredible example of the influence of the theories upon our appreciation of facts.

"Among the thousand reactions produced by the battery, this much is certain that there is not a single one

which can be adduced in support of dualism. Nevertheless, chemists who adopt this system have found means by their own interpretations to persuade themselves that all these various reactions prove that salts are composed of acid and oxide. The experimental proof is made daily in every course in chemistry. I was present lately at the lecture of a learned professor. Before him was placed a U-tube containing a solution of potassium sulphate colored with litmus. After having passed an electric current through this tube, and having pointed out that one of the limbs had become red and the other blue, the professor proceeded nearly in these words: 'You perceive in the most obvious manner that the sulphate has been decomposed; the red color of this limb proves to you that the sulphuric acid is transported to this side, whilst the oxide of potassium is carried into the other limb, which is consequently colored blue. Now, gentlemen, all salts are decomposed in the same manner, but nevertheless, in the presence of this glaring fact you will meet with persons who venture to deny in the sulphate the existence of sulphuric acid, or potash, and to reject the system of dualism.'

"What would the learned professor have said if one of his auditors had arisen and replied: 'By saying that all salts are decomposed in this manner, your intention is, without doubt, to teach us that such is the case with the great majority, but for my part, I think the contrary. I think that there is not a single one which is decomposed in the manner you describe, not even the one that is under our eyes. You yourself know very well that the hypochlorites, the chlorates, the perchlorates, the bromates, the nitrates and the salts of gold, platinum, manganese, lead, etc., give results differing extremely one from an-

other, and very different from that which you have just announced to us. With regard to the tube which is before us, it contains two substances, water and sulphate of potash, and at this moment one of the branches contains, not as you say sulphuric acid, SO_3, but instead, hydrogen sulphate, or rather, hydrogen potassium sulphate; in the other branch is found, not oxide of potassium but hydrate of oxide of potassium. So that under the influence of the electric current, there results, not a simple decomposition, but a double decomposition.' I remark, moreover, that this double decomposition occurs similarly when potassium chloride is decomposed in the presence of water. . . . Here are the facts but without hypothesis. By making use of hypothesis, however, we can prove anything we choose. We will first prove, with Davy, that potassium sulphate contains $K_2 . SO_4$. We therefore see that in reality, under the influence of the battery, SO_4 and K had separated from one another, and potassium, in the presence of water, decomposes it forming a hydrate, and the hydrogen of the water takes the place of the potassium which was set free.

"Let us now prove that Longchamp's theory is correct. We shall see that in reality, sulphuric acid separates from binoxide of potassium, and that under the influence of these two bodies an atom of water is decomposed. The oxygen unites with another atom of water to form the binoxide of hydrogen, which combines with the sulphurous acid to form hydrated sulphuric acid, while the hydrogen unites with the binoxide of potassium to form the hydrate of potassium. We could prove quite as easily that the sulphate of potash consists of $SK_2 . O_4$ or $S . O_4 . K_2$. Nay, more! Replace in your tube the sulphate of potash by sulphate of copper and at your pleasure you can cause

copper or oxide of copper to be decomposed at the negative pole, that is to say, you can at pleasure prove either the 'for' or 'against.'

"Lastly, we may say that it is not the salt at all, but the water that is decomposed by the action of the Galvanic current, and that the nascent oxygen and hydrogen decomposed the sulphate, the oxygen seizing upon the potassium and the hydrogen supplying its place.

"Let us, however, dismiss the battery and its reactions, because they can teach us nothing concerning the constitution of salts. What we have said above does not prove that sulphate of potash is not a compound of acid or oxide, but simply that we do not know what is the arrangement of the atoms in the salt."

After Berzelius proposed the theory of copulas, Gerhardt stated a theory in which he recalled the "radicals" but also followed the unitary notion contained in Dumas' older type theory. This he called the "theory of residues." It soon yielded to a newer and more satisfactory one. Neither Laurent nor Gerhardt was satisfied with the existing methods used in classifying compounds; and together they made the deductions upon which they based a new theory—the "type theory."

There is a wonderful and very intimate connection between the "radical theory," the "substitution theory," the "nucleus theory," the "older type theory" and this "new type theory." In the new type theory, there is unquestionably the idea of *unity*. Gerhardt declared that the dualistic idea had pertained, consciously or unconsciously, to some degree at least in all of the theories preceding Dumas' older type theory.

It becomes evident upon examination of this last proposition, that Laurent and Gerhardt were seeking light. Finally, the type theory was evolved by them. The two men were satisfied because they had found that for which they had been seeking, it was *unity*. This idea was the core of their type theory. There was also simplicity in this new theory, because around a few simple unitary types could be grouped all the complexities which had existed in the past, and simplicity was desirable. This theory, next to that of phlogiston, dominated chemistry the longest time.

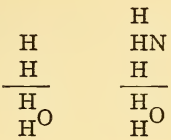
The master mind of the type theory is Gerhardt's. Laurent and Gerhardt proposed that compounds should be arranged in *series*, *each series being comparable to a type*. These *types* were of various classes. The *hydrogen type*, from which might be derived compounds like HCl and allied substances; this type also included the hydrocarbons. The *water type* and the *ammonia type*

$\begin{matrix} H \\ H \end{matrix}$ HYDROGEN TYPE $\begin{matrix} H \\ H \end{matrix}O$ WATER TYPE $\begin{matrix} H \\ HN \\ H \end{matrix}$ AMMONIA TYPE

Hydrochloric acid instead of being viewed as a derivative of the hydrogen type, was considered by some as a distinct type from which was derived chlorides, etc. The water type included the hydroxides, NaOH, KOH, etc., and most of the organic compounds. The ammonia type included a number of bodies, the amines, etc. Sulphuretted hydrogen was an auxiliary type yielding the sulphides.

This theory was criticised in that it still left the question concerning the formation of organic compounds unanswered.

Kekulé, in 1857, extended the type theory. He originated "mixed types." They were obtained by joining together two of the simple types:



These mixed types were used for the explanation of those compounds which could not be compared to the simple types. In this same year, Kekulé proposed an additional type—the methane or marsh gas type (CH_4). Many of the organic compounds were considered comparable to this type. But prior to this proposal of Kekulé came the assertions of Kolbe and Frankland.

Before 1857, Kolbe proposed a "new radical theory," in which he stated, "that the elements within the radical could be replaced by other elements. Organic compounds are all derivatives of inorganic, and result from the latter—in some cases directly—by wonderfully simple substitution processes."

Almost simultaneously with the preceding statements came this from Frankland, "that the copulation of radicals with elements depended upon a property inherent in the elementary atoms."

Kolbe agreed with Frankland's statement. Later, he wrote: "the combination of elements into radicals and into their various compounds is due to a property of the atoms of elements. This property is inherent in the atom. It is called the *saturating capacity* of the atom."

It had not been possible for chemists to explain why elements formed the *types* until Frankland, and more especially Kolbe, brought this "property of atoms" to their attention.

Kolbe continues, "The hydrogen atom has a saturating capacity of one, and the chlorine atom has a saturating capacity of one. They combine and form the *type* HCl. In the water type, two hydrogen atoms and one oxygen atom are united; that combination must be due to a saturating capacity on the part of the oxygen atom equal to two, whereby it is able to hold the two hydrogen atoms. In the ammonia type, there is a trivalent atom of nitrogen which has the power to hold three hydrogen atoms or three atoms of any other element having a saturating capacity of one. In the methane type, it is the saturating power of carbon, which gives rise to the class of bodies which can be constructed about a carbon atom or any other atom which has the power of saturating equal to four hydrogen atoms."

Frankland, at this time expressed his views as follows: "When the formulas of inorganic chemical compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony and arsenic, especially exhibit the tendency of these elements to form compounds containing three or five atoms of other elements; and it is in these proportions that their affinities are best satisfied. . . . It is sufficiently evident, . . . that such a tendency or law prevails, that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms."

Kolbe and Frankland are undoubtedly the originators of the idea of "valency." The attempt has been made in all subsequent writings upon this subject to ignore these two chemists and their ideas concerning the "saturating capacity" of the elementary atoms.

Kekulé disagreed with Kolbe's utterances. In his judgment the properties of compounds were not to be regarded as due primarily to the saturating power of the atoms of the various elements present in such compounds. At the same time (1857) as has been mentioned, he advocated the use of the *marsh gas or methane type*, giving to it the formula CH_4. Many chemists have ignored Kolbe in ascribing to Kekulé the discovery of the fact of the *quadrivalence of the carbon atom*. Later, Kekulé explained the combination of two carbon atoms, in this combination, he believed that each carbon retained its normal valence, two of the four affinity units of each carbon atom being neutralized in holding the carbon atoms together. This suggestion finally led to the *doctrine of the linking of carbon atoms*. Kekulé then intimated that "a more compact combination of carbon atoms" might be assumed to be possible.

The ideas of dualism and of copulas were passing and other theories were being formulated to replace them, and these succeeded, chiefly, because they were not too systematic. This idea of the "saturating capacity of atoms," proposed by Kolbe and Frankland and later by Kekulé and independently by Couper, gives liberty to chemists to formulate compounds guided by one thing only, namely, that the *atom possesses a definite saturating power*.

Kolbe suggested an additional thought, "that a compound derived from the 'water type,' possessing the

properties of hydroxides; or a compound derived from the 'ammonia type,' and possessing basic properties does not owe its character to the type from which it is derived, but obtains its characteristics from its component elements. The *elementary atoms* are to be regarded as the *true units* of a compound."

Couper developed the idea of the "saturating power of the atoms of elements" independently of Kekulé. In referring to Gerhardt's development of types, he objected to the vagueness of that idea as a means of classification, and especially opposed Gerhardt's opinion that the molecular constitution of bodies could never be ascertained by chemists. "Would it not be rational," says Couper, "in accepting this veto, to renounce chemical research altogether?" Couper believed that this dictum of Gerhardt was to be traced to the excessive employment of compound radicals, and to Gerhardt's ideas concerning the properties of these radicals. Gerhardt ignored the fact that these radicals can have no properties that are not a direct consequence of the properties of the individual elements of which they are composed, and hence, ascribed to them an unknown ultimate power which cannot be explained.

Chemists are, now, prepared to say with Kolbe, Kekulé, Couper and others of this time, that this so-called "saturating capacity" which Couper terms "chemical affinity" is a property inherent in and common to the elementary atoms.

Couper and Kekulé were so impressed with this idea of "affinity" that they distinguished between "affinity of kind" and "affinity of degree." Couper cited, as examples, the two oxides of carbon, CO and CO_2;—the former, he thought, expressed "affinity of kind," and the

latter expressed "affinity of degree"—the last degree—the ultimate affinity or combining power of the element carbon.

If there be a difference between the teachings of Couper and Kekulé, it is that Kekulé discriminated more clearly than Couper, between the "affinity of kind" and the "affinity of degree," or between *chemical affinity* and *basicity* of atoms. He clearly distinguished, and this has been too much forgotten in the later development of chemical affinity, between the "equivalent weight of the elements" and the "equivalency—saturating power—combining power of the elementary atoms."

Kekulé showed that this new theory, presented by him and Couper, was dealing with definite entities called atoms. These atoms or entities possessed definite properties. He did not deal with their unit weights. He was only concerned with the combining or substituting power of the atoms and he proposed that this power of the atoms be made comparable to the atom of hydrogen taken as *unity*. He demonstrated to his own satisfaction that the carbon atom was quadrivalent towards hydrogen. Further, that two atoms of carbon did not combine with more than six atoms of hydrogen; three with more than eight; four with more than ten, and so on.

Kekulé's paper, in which these thoughts appeared, was published, in 1858, in volume 106 of the "Annalen der Chemie." It is a contribution deserving very careful perusal and thought on the part of every student of chemistry. In that paper, Kekulé, not only called attention to the *quadrivalence of the carbon atom*, but he also laid the foundation stone of the modern hypothesis of *atom linking*.

Kekulé and Couper insisted that if a definite conception

of the connections between the properties and the structure of compounds is to be obtained, it must be based upon the study of the combining power, the saturating power, the valency of the elementary atom; for, remarks Couper, "the whole is simply a derivative of its parts."

Although the ideas of "radicals" and of "types" had been dismissed, Kekulé and Couper return in their discussion of "valency," to the four fundamental types: hydrogen or hydrochloric acid, water, ammonia and the methane type. With these as a basis, they developed the fundamental thoughts of their "theory of valency." In the first type (H_2), one atom of hydrogen is united with a second atom of the same element, in (HCl), one atom of chlorine is in union with one atom of hydrogen; in the second or water type (H_2O), one atom of oxygen is combined with two atoms of hydrogen; in the third, or the ammonia type (NH_3), one atom of nitrogen is in union with three atoms of hydrogen; and in the marsh gas type (CH_4) one atom of carbon is in union with four atoms of hydrogen.

How is the "valence" of the elementary atom to be expressed? The atom of chlorine, with reference to hydrogen as the standard, has the saturating capacity, the combining power, the affinity, the valency of one; the oxygen atom has a combining power, a valency of two compared with hydrogen; the nitrogen atom has a valency of three compared with hydrogen; the carbon atom has a saturating power of four. These atoms, chlorine, oxygen, nitrogen and carbon respectively are, as they were then said to be, univalent, bivalent, trivalent, quadrivalent.

A bivalent atom is one which combines with not more than two atoms of chlorine, bromine, or fluorine, and is, therefore, equivalent to another atom which combines

with not more than two atoms of hydrogen. In the same manner, trivalent and quadrivalent atoms are defined. When it is said that one atom is combined with a certain number of standard univalent atoms, direct interaction between these atoms in the molecule is assumed. When one atom of bismuth is combined with three atoms of chlorine, each of which is univalent, it is implied that in that molecule of bismuth chloride direct action of some kind occurs between the one atom of bismuth and the three atoms of chlorine. In marsh gas, one atom of carbon is in union with four univalent hydrogen atoms and it is assumed that in that gaseous molecule there is direct action and reaction of some kind between the one atom of carbon and the four univalent hydrogen atoms.

These points are familiar to all who have studied chemistry, and they may seem to receive unnecessary attention, but it must be remembered that the development of a chemical theory is being followed; and, hence, the aim must be to pursue the line of thought as developed by Kekulé and Couper.

What term shall be used to express the idea of the "saturating capacity of the atoms?" Affinity, equivalency, atomicity, saturating power, valency have been employed. "Valency" is to be preferred since it suggests no idea to which exception could be made. The terms, univalent, bivalent, trivalent, quadrivalent, quinquivalent, etc., have been developed and their application to atoms indicated.

How, then, are the atoms of chlorine, bromine, iodine and hydrogen equivalent? Kekulé did not imply, how much *by weight* of the elements was to be looked upon as equivalent. He emphasized, in all his writings upon this subject, that "equivalency" and "equivalent weight"

were not interchangeable terms. How, then, are these atoms equivalent? They are equivalent in this respect, that each combines with one and only one atom of hydrogen to form a gaseous molecule, for example, one atom of chlorine combines with one atom of hydrogen to form the gaseous molecule, hydrochloric acid gas, or one atom of hydrogen combines with a second atom to form a gaseous molecule of hydrogen. These atoms are equivalent and are to be regarded as standard univalent atoms.

The valency of the atoms of other elements can be determined by uniting them with these standard univalent atoms, and then determining how many atoms of the standards are present in the molecules of the products. It must be understood, however, the valency of the atom of an element cannot be determined accurately except at least one gasifiable compound can be prepared, composed of a single atom of the element in question combined with these standard univalent atoms and with such atoms only. For example, the valencies of copper and gallium cannot be determined unless gasifiable molecules of copper or of gallium and some standard univalent atom can be prepared. This accomplished, the valency of the copper and gallium will be the maximum number of atoms of hydrogen, of bromine, of chlorine, etc., with which the copper or gallium atom combines to yield gaseous molecules. A step further, the valency of an atom is a number which expresses the maximum number of standard univalent atoms, between which and the specified atom there is direct interaction in a gaseous molecule. This definition gives a working hypothesis which can be satisfactorily used in arriving at knowledge concerning the arrangement of molecules.

Can any definite meaning be drawn from the expres-

sion, the *carbon atom is quadrivalent* or *the carbon atom has four valencies?*

"The statement that an atom of carbon has four valencies, four units of affinity, cannot mean that the force of chemical attraction of a carbon atom is divided into four parts within the atom, the force has no meaning apart from two or more reacting bodies and here it is only one. Force is a name given by one of the parties to a transaction, but a transaction involves, at least, two transacting parties. But force between the carbon atom and another atom must vary with the external conditions, probably with distance, with the mass, and the chemical nature of both atoms.

"Then to give another view of it, the carbon atom has four valencies, four units of affinity. This cannot mean that four parts of the carbon atom are chemically active and the other parts inactive, such an hypothesis leads, at present, to contradictions. Moreover in the present state of our knowledge, it is inadvisable to hazard hypotheses as to the inner structure of atoms in order to explain these peculiar chemical phenomena or changes. Indeed, the atoms may not be homogeneous, but at present they are the ultimate particles to be considered in chemical changes.

"Again, the expressions under consideration cannot mean that the chemical energy of the carbon atom is divided or is always divisible into four parts. What is to be the unit of chemical work? The mass of matter fixed by a given atom? Where then is the equivalency between one atom of oxygen with the mass sixteen and two atoms of chlorine with the mass seventy-one? Let a carbon atom combine with four hydrogen atoms,—the total chemical energy of that carbon atom vanishes.

Let a carbon atom combine with two atoms of oxygen,—the total chemical energy of the uniting atoms again disappears. But if the carbon atoms possess four units of affinity, the oxygen atoms two units of affinity, and the hydrogen atoms one unit of affinity, the heats of formation of the compound molecules respectively ought to be equal. But the differences between the heats of formation of carbon compounds show that the expression 'carbon has four units of affinity' cannot mean that the chemical energy of the carbon atom is divisible into four parts, unless indeed the unit of affinity is variable and is varied for each combination of carbon with other atoms.

"The carbon atom has four valencies. Can this mean that the atom exercises force in four directions? The so-called valency then becomes a direction. But there is no force exercised until the mutual atomic transaction begins; the carbon atom considered alone has therefore no valencies. In the molecule CO: force is exercised by the carbon or by the oxygen atom; but the remaining valencies are sometimes said to be mutually satisfied. That is based on the present hypothesis, the carbon atom in the molecule CO exercises force in two directions on itself. But there again is the hypothesis of the non-homogeneity of the carbon atom and the existence of active and inactive parts in that atom. Further, in the vibration of a carbon atom there are four points, at each of which mutual action can occur between this atom and another atom. On this supposition, a double link would mean that mutual action occurs between the two atoms thus linked at two of these positions. The formula OCO would mean that in performing a vibration, the carbon atom acts twice and is twice acted upon by each oxygen atom. But if so, surely a double link would imply

molecular stability, whereas, it frequently means the reverse."

While a clear physical conception cannot be formed of the meaning of the phrase "the carbon atom has four affinities, four bonds," and although such formulas as OC, OCO, H_2CCH_2 and HCCH which spring from the notion of bonds, fail to call up in the mind clear images of the things they are meant to represent, nevertheless, it may be urged that inasmuch as the properties of such molecules show that chemical functions of the atoms of carbon vary in different molecules all of which are composed of carbon and hydrogen only, or of carbon and oxygen atoms only, it is convenient to express such variations of function in our nomenclature, and the expressions single, double, treble linked carbon atoms, are convenient for that purpose. The expressions single, double and treble linkings, mutual satisfaction of units of affinity, and the like, assume a knowledge, which at present is not possessed.

Is the valence of any one atom fixed or does it vary? To vary the valencies of atoms without proof for so doing, causes endless confusion and the applications of this hypothesis of valency become amusing exercises of fancy. The chlorine atom has the combining power or valence of one. Does this standard univalent atom ever present itself in a different rôle? Chlorine is a univalent atom compared with hydrogen; generally it is a univalent atom compared with oxygen, but an oxide of chlorine exists, having the formula Cl_2O_3, the derivatives of this oxide have been studied.

To satisfy the demands of the thought of a *fixed* valence,

this oxide must be graphically represented Cl–O–O–O–Cl, but many of the properties of this oxide do not permit a formulation of this description. Hence the question is urged, does the chlorine atom always possess a valency of one? Some of the compounds of iodine cannot be explained by maintaining the idea of a fixed valence for that element. As the elements are more thoroughly studied reasons for admitting the widening of the idea in regard to the saturating capacity of the atoms becomes more and more evident. The halogen atom is univalent when compared with the standard hydrogen, but when compared with oxygen, another saturating power is manifested. An atom of phosphorus compared with hydrogen is both trivalent and quinquivalent; the iron atom in its simplest combination with chlorine is bivalent, but with the same element it shows a higher combining power of three. Valence then is not fixed, it varies.

The chemists, who lived in the 60's were, of course, guarded in all their speculations concerning the combinations of atoms. They naturally felt, that if the properties of compounds were to be attributed to the nature of the atoms, then the saturating power must be a fixed value. They would not entertain any other idea.

Is it then surprising that at the present time students of chemistry have difficulty in convincing themselves of the variableness of valency? At first, it was taught that the valency of elements was as fixed as the laws of the Medes and Persians; to abandon that idea was to give up one of the articles of faith. The elements were arranged in groups with atoms of equal valency, as monads, dyads, triads, etc.; later, they were divided into two groups—those with even valencies and those with odd valencies. An odd valence could never change to an even, and an

even could never become an odd valence. Things have undergone a change since then. The early opinions in regard to the fixedness of this combining power of the atoms were modified. At first it was reluctantly admitted that valence may vary. But how? The elementary atom which had a saturating capacity of one, if it varied in its combining power or saturating capacity, became an atom with a saturating capacity of three, five, seven. The atom which had a valence of two, if it changed, became an atom having a valence of four, or six. Hence, the elements were arranged into two grand divisions: the *artiads*, those of even valencies, and the *perissads*, those of odd valencies. As time rolled on the article of faith was again modified. It was discovered that valency did not only vary from odd to odd and from even to even, but it varied from odd to even and even to odd. The valency of the iron atom changes from that of an artiad in ferrous chloride, to that of a persissad in ferric chloride, or from an even to an odd valence.

At the present time there are chemists who admit that the valency of an atom, its combining power, its affinity (using these terms in the sense in which they were used by Kekulé and Couper) not only varies—not only varies from odd to even and from even to odd, but further, that valence *is and may be anything*—depending upon the conditions under which the atoms of the elements happen to be placed at the time of their action and reaction. This is the most radical assertion that has been made during the years witnessing the development of the idea of valence, and yet chemists, some chemists, believe that it expresses the truth.

Examine the formula of arsenopyrite, FeSAs. Other examples from the mineral world might be placed with

this one. It is noticeable that the examples showing these peculiarities in valence are not found in the organic world; carbon, in its ramifications, combines principally with oxygen, nitrogen and hydrogen, and exhibits an invariable valence.

The valencies of atoms are graphically expressed in different ways. They were formally written, and even to-day may be seen written, in this manner, Cl^{I}, O^{II}, or with lines to left and right, as Cl—, —O—, O=C=O. Then followed an unconscious connection of symbols by means of lines, strokes, points, hooks or what not; so that compounds were looked upon as consisting of atoms hooked together.

The idea of units of affinity, or valency has been carried too far. It is very probable that the valency of the elementary atoms may be found to vary periodically with variations in the relative weights of these atoms. If this general statement is thoroughly established, the exact nature of the periodic function determined and the true atomic weight for each element fixed, then deductions may be drawn from the periodic law concerning valency.

Valency has been developed principally through the study of carbon and its derivatives; but as other elements and their combinations were examined difficulties arose. In looking over a broader field than that which was visible to the chemists of 1858 and the succeeding years, many facts were discovered not in harmony with the pronunciamento of Kekulé. The ideas concerning valence have changed until little remains of the original theory. What is the next step?

It must be remembered that these theories are merely

working hypotheses. Just as soon as they become inadequate, or fail to account for the phenomena being observed, they are laid aside and new theories take their place. And so with "valence."

Explanation of the Constitution of Chemical Compounds by Means of Physico-Chemical Processes.

DEVELOPMENT OF PHYSICAL CHEMISTRY.

The fact that an intimate relation existed between the chemical and physical properties of substances first appealed to the chemists of Lavoisier's time. Since then, investigators have sought to trace this relationship more completely. The laws of Avogadro and of Gay-Lussac are evidences of the investigations along physical lines; as are also the deductions of Dumas—determination of vapor density; of Dulong and Petit—law of specific heats; and of Mitscherlich—law of isomorphism.

These later chemists made use of physico-chemical methods in their researches, but, it remained for Hermann Kopp to be the real pioneer in the field of physical chemistry, in the discovery and use of physico-chemical processes for the determination of the constitution of chemical compounds.

In 1850, Kopp proposed a method whereby the "specific volume" of liquids could be determined. This investigation marks the *beginning of physical chemistry. Specific volume was found by dividing the molecular weight by the specific gravity of the liquid.* This discovery of Kopp is not epoch-making, but it is one step forward in the search

after truth regarding the constitution of chemical compounds. He observed that in many substances the differences in specific volumes were proportional to the differences in the structure of the compounds; and that the specific volumes of isomeric bodies were different. Those of the normal hydrocarbons, which were determined at the melting points, approached with an increase of carbon to a definite limit; and in the homologous series, he observed that for each additional CH_2 there was an increase of about twenty-two units in specific volume. Kopp thought it possible from such data to deduce from the molecular value of compounds the atomic volume of their constituent elements. He found eleven (11) to be the value for carbon, and 5.5 for hydrogen. Varying values were obtained for oxygen and nitrogen, the value apparently being dependent upon the manner in which the elements were combined. When oxygen was joined to carbon by a double bond in any chemical compound, it had a volume of 7.8; but when it was joined by a single bond it had a volume of 12.2. Kopp gave two values for sulphur, 12.2 and 20.6, the lower value being assigned to sulphur when it connected two elements; and the higher being assigned to it when it was saturating. He also discovered that metameric liquids generally possessed the same specific volume. It is evident, if the observations of Kopp are correct, that early in the sixth decade of the nineteenth century, chemists were beginning to find means by which they could determine the constitution of an organic compound.

It was possible, from the determination of the specific volume of a substance containing oxygen, to state whether that compound was an alcohol or a ketone. This was an advance in chemical knowledge.

Unfortunately, the observations of Kopp were permitted to go unnoticed for many years. Indeed, they received but little attention until Lossen gave them careful consideration. He conducted experiments along lines described by Kopp, and obtained for each increment of CH_2, in a series of monobasic acids, a value agreeing very closely with the constant first published by Kopp. In the primary alcohols, Lossen found that each additional CH_2 gave a numerical variation of from 18.7 to 21. He studied the propyl, isopropyl and allyl compounds and reported that in normal propyl and allyl compounds the CH_2 caused a variation of 5.5 to 5.9.

Later, Thorpe studied quadrivalent carbon atoms and their values in compounds, substituting chlorine in many of these for hydrogen, and discovered that the values for chlorine were, likewise, variable; he concluded, from his experiments, that the specific volume and also the boiling point of a hydrocarbon were changed by each atom of chlorine added to the compound.

From the studies of Thorpe and Lossen, the conclusion was reached that Kopp's deductions were only approximately true. They found, contrary to Kopp's assertions, that many isomeric bodies had different molecular values in unsaturated compounds. Each carbon doubly linked to carbon increased the molecular volume. A compound, containing carbon atoms in the form of a ring, possessed a smaller molecular volume than the isomeric bodies with an open chain, in which the carbon atoms were linked together by double bonds. Thorpe and Lossen demonstrated that the specific volume of substances was influenced by the *nature of the linking of the atoms*. Even when their atoms were similarly linked, isomeric bodies possessed different molecular volumes. Ethylene chloride

and ethylidene chloride show a difference of 47 in their molecular values, from which it follows that the molecular volumes of organic bodies are apparently conditioned by two influences: the one of an additive nature, which was observed by Kopp, the other of a constitutive nature, discovered by Thorpe and Lossen. After these two investigators had brought Kopp's deductions before chemists, others began to study his writings.

Kopp's experiments were conducted under conditions less favorable than those which a chemist of to-day meets in carrying out investigations of a like character.

Kopp was also the first chemist to point out the existing connection between the boiling point and the composition of compounds. He writes in his papers that he compared substances at their "boiling points." There is, however, no reason to believe that he corrected these for the lattitude in which he worked or for the pressure at which they were taken.

The results of Lossen and Thorpe differ from those of Kopp principally because the methods pursued by him were not strictly followed. He always used a peculiar style of distilling flask, and the bulb of the thermometer was placed on a level with the opening of the delivery tube and at the same time at a definite distance above the boiling liquid. The result will be different, if the thermometer bulb is in any other position or if the delivery tube is exposed to the air currents in the room. Kopp made no attempt to shield the delivery tube from the air currents in the room. The apparatus used by him was very different from that obtainable to-day. Thorpe and Lossen worked with entirely different and more refined instruments.

Before Kopp's discovery, an investigation of a compound gave only the weight of the elements in the compound in per cent. and this was the only data possible to obtain. Thereafter, the manner in which the elements existed in that compound could be determined. The determination of the specific volume indicated the presence of the hydroxyl group, made evident that all of the hydrogen of an alcohol was not alike—that one hydrogen atom was beyond the radical, and disclosed the condition—the linking—of the carbon in the compound.

Kopp's work possessed value; and a description of it constitutes the first chapter in physical chemistry.

Kopp sought to determine the specific volume of the natural sulphides, but his results led to no definite conclusion. Whether his investigations in this direction will be helpful in the solution of the molecular magnitude of these minerals remains to be seen. Every student of chemistry will find much that is instructive in Kopp's early papers, and they merit careful reading. They are to be found in the "Annalen der Chemie," Vol. 46, p. 212, Vol. 96 and succeeding volumes.

Some years after the preceding discovery was made, it was ascertained that a determination of the "molecular refraction" of substances gave valuable information concerning compounds. This was also a physico-chemical method. The results were interesting and demonstrated that a relation existed between the "optical behavior of solid and liquid substances and their chemical composition" between the composition of compounds and their

"refractive indexes." The co-efficient of refraction—the refractive index—the refractive quotient—for homogeneous light, passing from one medium to another, represents the ratio of the propagating velocities V_1 and V_2 in both media.

$$N = \frac{V_1}{V_2}$$

For single refracting media (in which similar optical deportment is observed in all directions) N is independent of the directions of the incident and refractive angles, therefore

$$N = \frac{V_1}{V_2} = \frac{\sin I}{\sin R},$$

a constant number for light of a definite wave length.

The specific refractive power or refraction constant

$$R = \frac{N^2 - 1}{(N^2 + 2) D_t}$$

in which D_t is the specific density of the liquid for the temperature t degrees and since

$$N = \frac{\sin I}{\sin R}$$

for light of definite wave length, then the molecular refraction for a particular substance will be found by using the formula:

$$R = \frac{(N^2 - 1) M}{(N^2 + 2) D_t}$$

the refractive power multiplied by the molecular weight of the substance. Molecular refraction is nearly the same in the case of compounds with isomeric positions, but it is dissimilar in the case of isomerides where the saturation of atoms is different, for example, in acetone and in allyl alcohol. Fortunately, the molecular refraction of a compound is approximately equal to the sum of the atomic refraction of the elements which compose it. The molecular refraction of a liquid carbon compound is equal to the sum of the atomic refractions.

At first it was believed that only one atomic refraction existed for each element in its compounds.

Landolt demonstrated that substances having the same refractive equivalents were probably the same. He writes: "The refractive equivalent depends upon the number of atoms in the molecule rather than on the arrangement of the atoms."

The refractive indexes of compounds were compared and it was found that the position or the linkage of the carbon atoms, as well as the hydrogen and oxygen present, caused differences in the molecular refractions. The refractive index of methyl chloride was found to be 13.2 and that of aldehyde 18.6. One carbon atom caused this difference. Acetaldehyde had a refractive index of 1.06, while the value for ethyl alcohol is 2.12; a difference of 1.06 caused by two hydrogen atoms. Between aldehyde and acetic acid there exists a difference of 2.5 in the refractive index.

From these and many other observations, which were made at the time, it was concluded that one carbon atom caused a difference of five (5) units in the refractive index if it were singly linked to another carbon atom; but with an oxygen atom it caused a difference of three (3).

Brühl continued this subject and, later, stated "Only the univalent elements have a constant atomic refraction, while the atomic refraction of the polyvalent elements, like oxygen, sulphur and carbon, is influenced by the manner in which these elements are combined one with the other." The group CO increased the refractive index of a compound more than oxygen singly combined. A difference of 1.78 in the refractive index is observed for carbon doubly linked to carbon. It became evident that important facts relating to the union of atoms in the molecule of carbon compounds could be learned from a determination of the refractive index of the molecule.

After studying benzene derivatives, Brühl concluded that in the benzene nucleus three doubly linked carbon atoms were present. The work of Brühl and Landolt was published in the "Annalen der Chemie."

Beginning with 1850, and continuing to the present time, efforts have been made to arrive at the constitution of compounds (organic, especially) from a study of their physical properties. Determinations of the refractive index and of the specific volume of organic substances have been helpful in denoting the configuration of the molecules. The refractive index of most of the minerals is known. Will not this information prove helpful in determining the composition of these inorganic complexes?

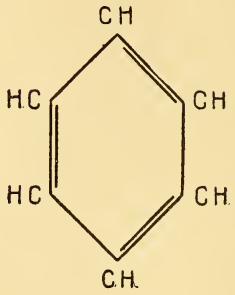
"Isomorphism" was not thoroughly understood when Kopp was conducting his experiments. Beginning with the year 1819, the subject received some attention. In 1820, the first hydrocarbons were discovered that illustrated this point. In 1830, Berzelius claimed "that

bodies of similar composition but possessing different properties were isomerides." And, in 1831, he distinguished between isomerides thus: "isomerism of bodies of different molecular weight was due to polymerism; of bodies of like molecular weight to metamerism."

The ideas concerning isomerism were not fully understood and it was felt that these should be applied with great caution. This field of investigation was new and much experimentation was required to perfect the knowledge of this branch of chemical science. These early ideas were more completely explained later. The further study of isomeric phenomena led finally to the establishment of a "theory of atom linking"—a "structural theory of chemistry." This theory was not only instrumental in explaining the cause of the innumerable isomerides, that had been observed before and after Kopp's age, but it was also helpful in enabling chemists to predict unknown compounds.

Kekulé had given a formula to express the saturated compounds of carbon—C_nH_{2n+2}. Concerning the carbon compounds which were poorer in hydrogen (the unsaturated compounds) he favored two views, namely, that a more compact union had occurred (a double, or treble linking of the pairs of carbon atoms), or that some of the carbon valencies were unsaturated. He assumed the presence of an "open chain" in the saturated compounds, and a "closed chain" or "benzene ring" in the unsaturated compounds. "In the latter each carbon atom in the molecule is united with a carbon atom. The structural formula which results is a hexagon—in the angles are placed the carbon atoms linked alternately to each other by one and two bonds, and each carbon atom is combined in every case with one atom of hydrogen or

with an atom of an element equivalent in combining power to hydrogen, thus:



From this formula he deduced a number of facts; the truth of these and other assumptions has since been verified. This work of Kekulé is frequently regarded as the pioneer work in "structural chemistry." Recall, however, the work of Gmelin.

Kekulé's "structural theory" thus successfully explained the constitution of the so-called "aromatic compounds." Kekulé, later, decided in favor of the idea that the carbon valencies were not all satisfied in these unsaturated or aromatic compounds of carbon.

Jacob Wislicenus had studied the lactic acids; and by his researches had added much to advance the doctrine of isomerism.

In 1860, Pasteur investigated the "optically active tartaric acids" and the inactive racemic acid produced by their combination. He thought that "optical activity" was probably due to "molecular asymmetry" and de-

pended, to some extent at least, upon the crystalline form of the substance.

Wislicenus, in 1873, wrote, "facts compel us to explain the difference of isomeric molecules of like structural formula by stating that the atoms take up a different arrangement in space." Did this statement of Wislicenus explain the existence of "optically active" bodies? This subject was being investigated and, in 1874, van't Hoff and Le Bel independently announced that the cause of "optical activity" was due to the presence in these substances of an *asymmetric carbon atom*—a carbon atom joined to four different atoms or radicals.

How were these atoms to be represented? They were arranged by van't Hoff at the corners of a tetrahedron having the carbon atom in the center. This idea of the arrangement of the *atoms in space* and *their rotation in space* was extended by Wislicenus. "The theory of stereo-chemistry—space chemistry" resulted.

This theory has been helpful in explaining the compounds of carbon. Will it not be applicable to certain inorganic compounds? Tin, cobalt, titanium, molybdenum, sulphur form compounds, many of which exhibit "geometrical isomerism."

Another physico-chemical method was proposed for the determination of the constitution of substances. The first attempts to determine the amount of heat liberated during chemical reactions had been made, and some idea of the affinities of the reacting substances had been deduced from the results; but exact relations of this nature could not be formulated until the heat changes were exactly measured. The method, now

proposed, consisted in exactly measuring the thermal changes occurring during chemical reactions and from the data obtained, deducing the chemical affinities active in the process. This method did not accomplish all that was expected.

Thermo-chemical data, are valuable in that they aid in ascertaining the strength of the current necessary to overcome chemical affinity. Julius Thomsen investigated from a thermo-chemical standpoint the formation of a number of salts. From the chemical value of copper sulphate, obtained by Thomsen, can be calculated the voltage necessary to decompose the compound and give the metallic copper.

However inadequate, thermo-chemical investigations have proven in the past, it is not unlikely that they may yet be found of value in the future in more perfectly elucidating the doctrine of affinity of the elements.

ELECTRO-CHEMICAL THEORIES.

The first electro-chemical theories were enunciated in the early years of the nineteenth century. In 1801, two Englishmen, Nicholson and Carlisle, had succeeded in increasing the efficiency of the volta battery to such a degree that they obtained a current from it capable of decomposing water.

In 1803, Berzelius and his student, Hisinger, published a paper in which they described the decomposition, by means of an electric current, of certain salts into their bases and acids.

In 1800, Sir Humphrey Davy began his investigations of the action of the current on chemical compounds,

and in 1807, obtained a sufficiently strong current from the volta pile to decompose caustic potash and caustic soda, and in 1808, the hydroxides of calcium and barium, obtaining their corresponding metals. These were valuable discoveries in the judgment of Berzelius.

In 1807, Davy announced the first "electro-chemical theory," in which he expressed the belief that bodies having an affinity for one another were in different electrical states, and that chemical and electrical attractions depended upon the same cause, acting in the one case on particles and in the other on masses of matter.

After these observations were made, it was but natural for chemists to make every effort to identify chemical affinity with electricity.

In 1812, Berzelius brought forward the main points of his "electro-chemical theory," page 90. He stated that a relation existed between chemical and electrical processes. Electric fire, Berzelius thought, was the same as fire originating from chemical combustion, because the electric spark will heat, melt and ignite all combustible substances and volatile metals. Prolonged action of the electric spark heats water to boiling and solids to redness. Carbon in a vacuum will be made to glow by a current from an electric battery and the same action is observed as carbon burning and oxidizing in the air. Combustion was, therefore, an electro-chemical phenomena, and all phenomena not satisfactorily explained by heat could be explained by means of electricity.

Concerning the current obtained from the volta pile—Volta thought that metal contact was the cause of the current; while Davy contended that "electric condition increases in proportion to the affinity of the two metals acting. Temperature also influences electric condition."

Assuming that substances were composed of atoms, Berzelius believed that these ultimate particles of matter possessed "polarity" upon which the electric phenomena shown by the atoms was dependent. He believed that each atom was inherently "electric" and that this electricity passed to two opposite poles—each atom, therefore, possessing two kinds of electricity—the one pole being electro-positive and the other being electro-negative. Later, Berzelius stated that the quantities of electricity of the atoms of elements were different, so that elements were *either* electro-positive or electro-negative depending upon the preponderance of one kind of electricity over the other in the atom.

According to this idea of *unipolarity or one-sidedness*, an atom possessed two kinds of electricity, but if the positive was in the greater degree the atom became known as an electro-positive atom, and if the negative was in the greater amount the atom was then known as an electro-negative atom. Berzelius, therefore, divided the elements into two groups:—electro-positive and electro-negative elements according to their prevailing electricities. He also extended this idea to embrace compounds.

Berzelius' "electro-chemical theory" was first published in Sweden in 1814, in France in 1819 and in Germany in 1820. It dominated chemical thought from 1820 to 1840.

Berzelius and Hisinger had conducted a current through a solution of sodium sulphate, contained in a V-shaped tube. The contents of both arms of the tube were tested after the current had been passed. With litmus, the contents of one arm gave the *red of acids* (hence electro−), and the contents of the other arm gave the *blue of bases* (hence electro+). In other words, by the decomposition

of sodium sulphate, by the electric current, the salt had been separated into its component parts $Na_2O.SO_3$. Potassium sulphate, similarly, gave $K_2O.SO_3$. The metallic oxide in both instances, was the positive constituent of the salt, whereas the oxide of the non-metal (SO_3) was the negative constituent of the salt. These two electrified components, when combined, gave rise to the salt, neutral in its chemical reaction. Berzelius concluded, from these experiments, that salts consisted of *two distinct parts* (a basic and an acid portion) electrically different. In consequence of the above conclusion, he formulated his "dualistic theory," page 89.

Berzelius believed that when two bodies are acting electrically and fire appears, the current ceases. When two opposite electricities unite, the union is accompanied with a spark; when substances have combined and are no longer electric (they being neutral) and are then separated, the elementary atoms again take on their original electricity. Chemical union occurs because of the union of different electricities, and in every chemical union there is an explanation for combustion. There is a neutralization of opposite electricities, which neutralization produces fire and heat, as well as light. Substances after combination, remain in the compound with an electric force greater than any force which would bring about a mechanical separation. Was this force inherent in the atoms or was it a property of electricity? This question troubled the great master.

In the classification of elements and compounds according to their electricities: Oxygen and the other non-metals were placed in the electro-negative group. Hydrogen and the metals were arranged according to the strength of their electrical affinities in the electro-positive group.

Acid oxides were placed in the electro-negative group and basic oxides in the electro-positive division. Salts were also classified—those which united to form new compounds—to-day called "double salts," for example, $MgO.2Na_2SO_4$ and $PtCl_4.2KCl$ as electro-positive and electro-negative.

How does electricity exist in these bodies? How can a substance be electro-negative or electro-positive? These were questions presenting themselves, not only to Berzelius, but to all others. Berzelius stated that substances were not only electric but they must be electric to their minutest particles—the atoms. This thought gave rise to the "theory or philosophy of electro-chemistry—or the corpuscular theory."

But specific "unipolarity" did not serve to explain all of the phenomena, so that it was concluded that chemical union depended upon the *intensity* of polarity. The affinity of elements was an expression of their particular electricity.

These were, briefly, the views held by Berzelius. His "electro-chemical theory" differed from the "electro-chemical theory" of Davy. It was Davy's belief that the *atom* was *electrically neutral* and acquired either its positive or negative charge of electricity by *contact* with other atoms.

From 1820, when Berzelius' idea began to be widely discussed, until 1840, he fought for his electro-chemical theory; upheld at first by Wöhler and Liebig. But, when ideas and facts grew too numerous, particularly in the organic field, to make its further acceptance possible, Berzelius modified and remodified it from time to time until in 1840, it received its death blow.

The first criticism which Berzelius' electro-chemical

theory received was, if chemical union is produced by the electrical attraction of oppositely charged atoms alone, then, when these atoms come together, their electric differences would disappear, and in consequence, the compound would fall apart; or as soon as the atoms separated, they would take up their respective electricities, and would, therefore, immediately recombine; hence, compounds would always be in the state of unstable equilibrium and complete decomposition would be almost impossible.

A second objection to this theory was, if chemical union depended only upon electrical attraction, then the properties of the compounds must depend upon the nature of the charges existing in the atoms in the compounds; therefore, when it was found to be possible to substitute three atoms of chlorine for the three atoms of hydrogen in acetic acid, and further that the properties of trichloracetic acid were almost identical with the properties of acetic acid, facts were being obtained which were opposed to Berzelius' theory. This was the chief objection against this theory.

Recall the recent work of J. J. Thomsen, page 102, who, having electrolyzed hydrogen, found some hydrogen at the negative pole and some at the positive pole. The important point, then, is that hydrogen is not always positive. The chlorine derivatives of methane were investigated and it was concluded that the chlorine in these compounds was charged with the same kind of electricity as that possessed by the hydrogen which the chlorine had replaced. If these observations are true then the chief objection to the theory of electro-chemistry of Berzelius is left without a foundation.

Following the enunciation of the electro-chemical theory by Berzelius, the next important advance in electro-chemistry was made by Faraday. He showed the identity of electricity from different sources; and investigated the relation existing between the amount of a compound decomposed by the current, and the amount of the current used. He found that the two were proportional to one another and announced his "law of electro-chemical equivalents" in consequence. "The amount of chemical decomposition effected by the passage of the current is proportional to the amount of electricity which flows through the conductor."

Faraday passed the same amount of current through a number of different metallic salt solutions. His conclusions were these:—"The amounts of the different elements which are separated by the same quantity of electricity bear the same relation to one another as the equivalents of these elements. The atoms of all univalent elements carry exactly the same quantity of electricity—of bivalent elements twice as much, of trivalent three times, and so on. In a word, all atoms have either the same capacity for electricity, or a simple rational multiple of the capacity of the univalent atoms."

Faraday is also the author of the system of nomenclature used to-day in electro-chemistry.

At this point, a digression will be made in order to trace the development of ideas concerning "solution" and the connection of these ideas with the notions of electro-chemistry:

It had been early observed, that to have chemical action one body must have motion, must be mobile, so that one

reacting substance, at least, could present its polarity to the other. Heat is required to unite most gaseous bodies. If the particles are driven too far apart, however, they will not unite because they have lost their power of electro-chemical activity. Union between solids does not often occur, but takes place when one of the solids is dissolved and more readily when both are brought into solution. An old chemical expression arose "Corporanon agunt nisi liquida." Liquid bodies act on each other when surfaces exposed are large.

Solutions:—First, a solution in the broadest sense of the word is a homogeneous mixture which cannot be separated into its component parts by simple mechanical means. Powders and emulsions which may be with very little expenditure of time and labor resolved into their constituents by lixivation, subsidation and the like are not solutions. A solution exists only when there is a complete and mutual interpenetration of the individual constituents, that is an interpenetration which extends down to the molecules themselves.

Solutions are of three kinds,—gaseous, liquid and solid.

Solution of Gases:—Gases mix in every proportion and interpenetrate one another completely, so that gas mixtures are always gaseous solutions. The pressure P of a mixture of gases is equal to the sum of the partial pressures p', p'', etc., of the individual constituents.

Solution of Gases and Liquids:—By absorption, gases unite with liquids to form liquid solutions. From Henry's law, it is inferred that the quantity of gas taken up by a liquid is proportional to the pressure under which that gas exists.

Solution of Liquids:—Liquid solutions may be arranged into two groups: first, those in which the constituents

mix in every possible proportion; second, those in which the components are only partially soluble one in the other. Group I is illustrated by pairs of liquids such as water and alcohol, carbon bisulphide and alcohol. Group II, by water and aniline, or water and acetic ether. It is altogether probable that there is no deep-seated difference between the two groups, because every pair of liquids has its critical point beyond which the pair of the one group may belong to the one above or to the one below.

The properties of solutions of liquids in one another cannot, as a rule, be calculated out beforehand, as in the case of gases, from the properties of their constituents. In mixing liquids, there are always contractions, the volume of the mixture is not equal to the sum of the volumes of the components. Again, changes appear in color, in refraction, in specific heat, and the like, which changes do not often correspond with those calculated from the rules laid down for mixtures.

Solution of Solids:—Solid solutions are produced when the substance to be dissolved penetrates into the pores of the solid, for example, iodine into starch. Solid solutions are often produced when liquid solutions congeal or when crystals separate from solutions. The color of crystals may also be included under this head of solid solutions.

Dilute Solutions:—The behavior of dilute liquid solutions is of very great theoretical importance. In such solutions one of the components (the solvent) is, in comparison to the other (the dissolved substance) in very great excess. This example illustrates the point—

If a layer of pure water is poured over a sugar solution, the two layers will gradually mix because the sugar must pass from points of a higher concentration to points of a lower concentration, that is, it wanders upward, and eventually there results a dilute sugar solution; but, if a semi-permeable diaphragm were placed between the layers of pure water and a sugar solution, the penetration of the sugar from the lower layer to the upper layer may be prevented. Such a diaphragm may be constructed in various ways. The most familiar method consists in saturating a porous plate with copper sulphate solution and then dipping it into a solution of potassium ferrocyanide, there results in the pores of the plate a reddish-brown precipitate of copper ferrocyanide, which becomes the membrane, or diaphragm, preventing the passage of the dissolved sugar from one liquid into the other but permitting the passage of water.

The sugar molecules, which still have the tendency to pass from their solution into water, that is, to diffuse into the water, are prevented from so doing by such a membrane and naturally exert upon it a pressure, which pressure has been called "osmotic pressure;" this has been measured by Pfeffer. A porous cup had formed in it a copper ferrocyanide membrane, and there was poured into it a sugar solution, the membrane hinders the outward passage of the sugar molecules. The porous cup was then closed with a stopper carrying a manometer and introduced into water, the water presses inward, exerts a pressure on the interior of the cup upward indicated by the manometer, which pressure represents the osmotic pressure of the sugar solution. The osmotic pressure for a four per cent. sugar solution is greater than the pressure of a quarter of an atmosphere.

Nernst has suggested certain principles which take into consideration the influence exerted by the nature of the solvent upon the osmotic pressure. If two solvents are used which are only slightly soluble in each other, the dissolved substance distributes itself in a constant ratio between the two solvents. Hence it was concluded that the osmotic pressure was independent of the nature of the solvent.

This principle, other physical chemists contend, is only of value in the form in which it has been given with this proviso; that there is an equal molecular weight of the dissolved substance in both solutions; if that be not the case then Nernst's principle must be changed.

If the temperature remains constant, the proportion between the pressure and the molecular weight will remain definite. Osmotic pressure increases with temperature. For all substances which are similarly dissolved, the increase of pressure per degree is the same as that observed for gases, so that the osmotic pressure formula is

$$P = P_o\left(1 + \frac{t}{273}\right) = P_o(1 + 0.003665t),$$

in which P is the pressure at t for zero degrees or $t = 273$. The osmotic pressure of a sugar solution is just as great as the pressure which that sugar would exert if it could occur as a gas in the same space occupied by the solution.

What has been said for sugar in solution applies universally to all dilute solutions.

The hypothesis of Avogadro can be applied to dilute solutions,—"solutions which at like temperatures have like osmotic pressures in equal volumes contain the same number of molecules of dissolved substances." Such

solutions show equal elevation in boiling point, equal reduction or lowering in the freezing point, and the degree of elevation or the degree of lowering is dependent upon the number and not upon the nature of the molecules of the substance dissolved.

A more complete exposition of the foregoing facts will be found in the "Zeitschrift für physikalische Chemie," 1, 481 (1887), in an article entitled the "Roll of Osmotic Pressure in the Analogy between Solutions and Gases," by van't Hoff.

To show how Avogadro's hypothesis is confirmed by the deportment of solutions, van't Hoff in that article offers the following experiment made with a one per cent. sugar solution, that is, a solution of one gram of sugar in one hundred grams of water. It has, therefore, one gram of sugar in about 100.6 cc. of solution. If the osmotic pressure of this solution be compared with the tension of some gas, like hydrogen, which contains just as many molecules for the 100.6 cc., it is discovered that there is a most astonishing concordance in the result. Pfeffer found that such a solution at 0° gives a pressure of 0.649 atmosphere. As hydrogen at one atmosphere weighs per litre 0.0896 gram and the preceding concentration gives 0.0581 gram per litre, then the pressure for the hydrogen for similar concentration and at 0°, calculated from the gas laws, equals 0.656 atmosphere, which compares favorably with the value 0.649 atmosphere obtained for the sugar. Investigations were similarly conducted at other temperatures and the conclusion was reached that the osmotic pressure directly deduced from a sugar solution is at the same temperature or at like temperatures nearly equal to the tension of a gas, which contains just as many molecules as there are sugar molecules in the same volume of the solution.

This is experimental work, comparing a sugar solution with a gas, hydrogen. Similar experiments were conducted with malic acid, tartaric acid, citric acid, magnesium malate, invert sugar and the results were very concordant.

Among gases there are certain irregularities due to dissociation phenomena, so too, there are exceptions to these observations on the part of certain other substances which are dissolved and these exceptions are particularly noticeable among acids, bases and salts which show remarkable and, at times, very great variations.

From this work—the step to the consideration of the action of the current of electricity upon dilute solutions, is but a natural one.

It will be recalled that the power of the current to decompose chemical compounds had been made prominent by the work of Faraday. *Electrolysis* is the term applied by him to this phenomena. Some of the most interesting advances made in electro-chemistry have been along this line of inquiry. Upon immersing the two poles of a voltaic cell into water containing a small quantity of sulphuric acid, hydrogen will be liberated at the one pole, and oxygen will appear at the other. Davy conducted an experiment to prove that the hydrogen and the oxygen liberated had not come from the same molecule of water. The action of the current upon other chemical compounds has been briefly set forth. Various theories were suggested from time to time to account for the reactions taking place; the last of these is the "theory of dissociation of substances dissolved in water," by Svante Arrhenius.

Arrhenius, a Swede, was attracted by the relations existing between solutions and gases—the work of van't Hoff, and in the "Zeitschrift für physikalische Chemie," Vol. 1, 631 (1887), published an article (translated) upon the dissociation of solids in water, in which he attempts to prove that salts, acids and bases manifest a higher osmotic pressure, than they are entitled to if the hypothesis of Avogadro for dilute solutions is applicable to them. It must be admitted for such solutions that the water exerts an influence which tends, so to speak, to destroy the molecules; in other words, the molecules of salts, bases, and acids, it must be granted, are separated into fractions, and these parts no longer conduct themselves in the manner noticed with sugar dissolved in water. Arrhenius believed that only those substances, which were decomposed into fractions upon solution in water conducted the current. Such substances he termed *electrolytes*. In the case of electrolytes there is every reason to believe that the original substances have, by solution, been dissociated; that the molecules of these bodies conducting the current have been broken down in aqueous solution into parts which are positively and negatively charged; and that these parts behave like distinct independent molecules, which Arrhenius called *ions*, those having the *positive charge* were called *kations*, those having the *negative charge*, *anions*.

If the kations migrate in one direction and the anions in the other a transportation of electricity occurs, or, in other words, there is produced an electric current, so that the direction of the current is connected with the presence of ions traveling about in the solution.

Naturally these groups in their ionic condition have properties very different from those which the atoms

possess in their neutral state when they are free from electricity. Arrhenius sought to explain this—Dilute hydrochloric acid consists in addition to undissociated molecules of hydrochloric acid—positively charged hydrogen and negatively charged chlorine ions. The hydrogen kations swimming about in the hydrochloric acid manifest, in consequence of their similar charge, no desire whatever to combine with one another and to escape as hydrogen gas, H_2; on the contrary they tend to repel one another and it is only after they have lost their charge that it is possible for them to recombine. This happens when an electric current is sent through the liquid. In the passage of that current the hydrogen kations, which are present collect about the negative electrode, give up to that electrode their positive charge and pass back into electrically neutral hydrogen atoms which quickly combine by twos and escape in the form of hydrogen gas, H_2. This also applies to the chlorine anions excepting that they lose their negative charge at the positive electrode where chlorine appears.

The ions H and Cl, dissolved in water do not possess the same properties as the gases H_2 and Cl_2. In the hydrochloric acid the dissociation is into $H+$ and $Cl-$; the number of the negative chlorine ions is always equal to the number of the positive hydrogen ions. Inasmuch as hydrochloric acid in its ordinary state is completely non-electric, and as consequently the sum of the discharges of all the ions that can be present in it are absolutely equal to zero, then the absolute value of the positive charge of a hydrogen kation must be as great as the negative charge of a chlorine anion, so that the chlorine and hydrogen ions are not only chemically but they are also electrically equivalent to each other. If the current be

sent through hydrochloric acid, for every atom of hydrogen set free at one electrode there must be an atom of chlorine liberated at the other. If this were not the case, if more hydrogen was liberated than the equivalent of chlorine then there would be in the liquid more positive than negative electricity and that liquid would have a negative charge, whereas in reality hydrochloric acid is completely neutral, electrically speaking. The same is true of hydrobromic acid and hydriodic acid and, according to this ion theory, an acid is an electrolyte consisting of hydrogen kations. A base is an electrolyte that contains hydroxyl anions. An acid gives as many hydrogen ions as it has basicity. The haloid acids are monobasic and they yield but one hydrogen ion; the dibasic acids dissociate into two hydrogen ions. Acids dissociate into hydrogen ions and a radical, for example, sulphuric acid dissociates into H ions (two of them) and into the (SO_4) radical; the charge of the (SO_4) anions is equal to two times (e) where (e) represents the charge of H. All that has been said about acids holds true of bases.

Salts dissociate into metal kations and acid radical anions. The magnitude of the charge may be calculated. A silver ion is equivalent to a hydrogen ion, both have the same charge. By the passage of an ampere of electricity, which is called a coulomb, through a silver salt solution Kohlrausch says that 0.001118 gram of silver will be separated, the quantity of silver divided by the atomic weight of silver will give the gram equivalence of silver having a charge of one coulomb, whence it follows that the charge of one gram of silver or a gram equivalent of silver equals 96540 coulombs, and for a gram equivalent of an ion the charge (e) is equal to the

number 96540 coulombs; the absolute value of an electric charge for an ion, therefore, might equal 8×1020 coulombs.

The ions can move and wander about, or migrate, as it is termed. They have a velocity of migration.

The essentials of the various chemical theories have been presented. No study of chemistry is complete without a knowledge of these landmarks of chemical science.

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